ANNUAL PROGRAM REVIEW

CHEMICAL PULPING AND BLEACHING

March 24, 1997

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CHEMICAL PULPING AND BLEACHING

March 24, 1997 Agenda

ANNUAL PROGRAM REVIEW

1:00 Introduction/Committee Assignments

1:10 Chemical Fundamentals of Bleaching (Project F015/4168/Thesis Research)

- NMR/Peroxide Bleaching/Hexenuronic Acids — Art Ragauskas
- Laccase Bleaching — Jim Sealey
- Ozone Bleaching — Don Dimmel

2:35 Break

2:45 Environmentally Compatible Production of Bleached Chemical Pulp (Project F013/4120/Thesis Research)

- Bleachability Studies — Tom McDonough
- Extended Oxygen Delignification of High Yield Pulps — Storker Moe

4:00 Break

4:10 Closed Mill Operations (Project F017)

- Metal Binding in Wood Pulps — Alan Rudie
- Modeling of Non Process Element Equilibria — Jim Frederick

4:45 Break

4:50 Pulping Studies (Project 4120/3661)

- Measurement of AQ in Pulping Liquors — Clark Woitkovich
- Catalysts-from-Lignin — Don Dimmel

5:20 Adjourn

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PAC MEETING

8:00 Discussion of Projects/Future Directions — Paul Wollwage

12:00 Adjourn

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Environmentally Compatible Production of Bleached Chemical Pulp

PROJECT SUMMARY

Date:	March 16, 1997
Project Title:	ENVIRONMENTALLY COMPATIBLE PRODUCTION OF BLEACHED CHEMICAL PULP
Project Staff:	T.J. McDonough, C.E. Courchene, A. Shaket, N. Rawat, S. Moe, A. Ragauskas,
Budget (FY 96-97):	$388,950
Division:	CBSD
Project Number:	F013

Objective

Define pulping and bleaching technology that will decrease or eliminate the release of byproduct organic chlorine compounds without sacrificing bleached pulp quality.

Goals

1. Establish measures of bleachability at constant unbleached kappa number and use them to identify kraft pulping variables that determine bleachability.

    a) Identify residual lignin structural features likely to be of importance in defining bleachability

2. Improve the performance of elemental chlorine free bleaching sequences based on chlorine dioxide.

    a) Confirm benefits of short retention time chlorine dioxide delignification.

    b) Determine optimum pH for the D_1 stage in ECF sequences

3. Improve the performance of delignification and bleaching methods based on the use of compounds that contain no chlorine.

    a) Determine rate laws governing the kinetics of delignification and cellulose degradation by ozone, as a route to improved selectivity in ozone bleaching.

b) Identify optimum conditions for delignification with combinations of oxygen, hydrogen peroxide, magnesium sulfate, cyanamide and DTMPA

c) Establish effects of delignification with kraft pulping liquor, oxygen and ozone on cellulose characteristics (viscosity, carboxyl content, etc.), pulp refining behavior and papermaking properties, and compare with corresponding effects of delignification with chlorine and chlorine dioxide.

4. Identify bleaching processes and conditions that minimize the potential for environmental effects.

a) Compare toxicity of effluents from chlorine dioxide delignification with that of effluents from delignification with chlorine

Summary

Recent activity in this project area has included research on the relationship between pulping conditions and bleachability, improvements to elemental chlorine free (ECF) bleaching sequences, chlorine compound free delignification and bleaching and characterization of bleach filtrates with regard to potential for environmental effect.

Work on relating softwood pulping conditions to bleachability has investigated the effects of effective alkali (EA) charge, sulfidity and anthraquinone. Work has also been initiated on a more global study of the influence of pulping variables and their interactions on subsequent bleachability in both oxygen-based and ECF sequences. In the $D_0(EO)D_1$ sequence, increasing EA increases brightness ceiling and decreases the amount of ClO_2 needed for a given brightness, while decreasing the kappa number has a similar effect. Effects of EA after full bleaching are more subtle. At normal unbleached kappa numbers, increasing EA increases the brightness ceiling. Addition of anthraquinone (AQ) had a barely noticeable negative effect on the brightness ceiling, but soda and soda-AQ pulps had significantly (2-3 points) lower brightness ceiling than the corresponding kraft and kraft-AQ pulps.

Research directed toward improved ECF sequences has been centered on two objectives: confirming the benefits of a very short retention time chlorine dioxide delignification ("D_0") stages and elucidation of the pH dependence of the performance of the first chlorine dioxide brightening ("D_1") stage. Previous work has demonstrated the potential of short retention time D_0 stages to reduce capital investment and formation of chlorinated organic byproducts. Planning of a larger scale trial is underway. An extensive systematic study of the effect of removal of chlorine from the bleaching sequence on the pH dependence of the D_1 stage is well underway.

The objectives of the research done on nonchlorine delignification and bleaching have been (1) to determine the kinetics of delignification and carbohydrate attack by ozone, as a route toward

ozone bleaching systems having improved selectivity, (2) to investigate delignification by combinations of oxygen and hydrogen peroxide in the presence of potentially beneficial additives (cyanamide, DTMPA and $MgSO_4$) and (3) to investigate process alternatives involving extended delignification by oxygen after kraft pulping and several of its modifications. In addition, a proposal is in preparation to investigate the effects of of lignin removal by extended kraft pulping, oxygen, chlorine dioxide and chlorine on refinability and intrinsic fiber properties. This work will be a collaboration between the Pulping and Bleaching, Wood Chemistry and Paper Physics Groups.

Relevant information on the stoichiometry and kinetics of ozone delignification of southern pine kraft pulp has been developed. The amount of ozone consumed per g of lignin removed was found to be 0.13 g. Lignin removal from brownstock was shown to proceed at a constant rate over the range studied. Oxygen delignification accelerated subsequent ozone delignification and made the rate time dependent.

Research on oxygen-peroxide delignification of pulp of kappa number 100 from old corrugated containers showed that addition of neither DTMPA nor cyanamide was cost effective. Optimization of the oxygen-peroxide stage followed by AODODED bleaching gave higher brightness and much lower chlorine dioxide consumption than a control DEDED sequence.

Research on environmental effects of bleaching filtrates has been done in the form of Ph.D. thesis research on the toxicity of filtrates from chlorine and chlorine dioxide delignification sequences after oxygen delignification. Ageneral conclusion was that, by most assays, the chlorine dioxide filtrates were not significantly toxic. The toxicity revealed by more sensitive assays appeared to not to originate in the bleaching stages and was usually attenuated at higher oxidant charges.

Introduction

The current report is a brief summary of activity on this project over the past year. A more complete Member Company report is in preparation and will be completed before June 30, 1997.

Bleachability Studies

The main goal of our research on kraft pulp bleachability is to identify and exploit relationships between kraft pulping conditions and bleachability, defined as the ease with which pulp of a given kappa number can be delignified and brightened. A secondary goal is to identify pulp characteristics capable of being measured relatively easily that can serve as indicators of bleachability. Our work on kraft pulp bleachability has received additional support through funding by the U.S. Department of Energy, and relevant results of the DOE-funded work are included in this report.

Pulping Conditions and Bleachability

We showed earlier[1] that higher-kappa pulps and pulps prepared under simulated EMCC® conditions are more readily delignified in the $D_0(EO)$ partial sequence than pulps prepared under conventional kraft pulping conditions, and that the results may be explainable in terms of condensed aromatic units and interunit ether linkages within the chemical structure of the residual lignin in the pulps. We also showed that, in the D_1ED_2 bleaching of these pulps, the brightness ceiling increased with increasing levels of brightness entering the D_2 stage and was higher for modified than for conventional pulps. These results demonstrated that the bleachability of kraft pulps can be affected by changing pulping conditions, but did not allow specific effects to be associated with individual pulping variables. In subsequent work, we have begun to study effects of individual pulping variables. Initial emphasis has been on effective alkali (EA), because of indications in the literature[2] that it has an effect.

Effective Alkali, Unbleached Kappa Number and Bleachability

Preliminary work on the effect of EA charge during pulping on the bleachability of southern pine kraft pulp was described earlier.[3] The results obtained up to the time of that report indicated that, at high unbleached kappa number (27-28) high alkali pulp was more difficult to bleach than low alkali pulp, but at low kappa number (13-14) the reverse was true. It was hypothesized then that under high alkali, high kappa conditions, the residual lignin had not been exposed to pulping liquor enough to undergo beneficial fragmentation reactions that did occur when the cook was extended to a lower kappa number in the presence of excess alkali.

Subsequent experiments on newly prepared pulps, however, did not confirm this observation. It was then deemed prudent to perform a systematically designed experiment incorporating replication, not only of the bleaching experiments, but also of the pulping experiments that provided the pulp to be bleached. From a statistical standpoint this is necessary to be able to allow the effects on bleaching to be evaluated in the light of the experimental variability between pulping runs. In other words, this is necessary to allow any observed effects on bleaching to be unambiguously associated with the changes in pulping variables.

Response in the $D_0(EO)D_1$ Partial Sequence

Table 1 shows the results of the pulping runs done to provide the pulps for bleaching and identifies the four conditions as low kappa, low alkali (LKLA), low kappa, high alkali

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[1] Froass, P.M., Ragauskas, A.J., McDonough, T.J., and Jiang, J., "Relationship Between Residual Lignin Structure and Bleachability," paper presented at the 1996 International Pulp Bleaching Conference, Washington, D.C., April 15-18, 1996.

[2] Carno, B., Norrstrom, H., and Ohlsson, L., "The influence of Cooking Conditions on the Bleachability of Pine Sulphate Pulp," *Svensk Papperstidn.* (4):127(1975)

[3] McDonough, T.J., IPST Chemical Pulping and Bleaching Annual Program Review, March 20, 1996, pp. 125-175.

(LKHA), high kappa, low alkali (HKLA), and high kappa, high alkali (HKHA). Table 2 gives the results of bleaching in the first 3 stages of the $D_0(EO)D_1ED_2$ sequence, with a kappa factor of 0.20 in the D_0 stage. As expected, the low kappa pulps consumed significantly more oxidant per unit of kappa number reduction in the first two stages. Although the unbleached brightness was somewhat more variable than expected, the brightness of the high alkali pulps was significantly (2 points) higher than that of the low alkali pulps after the first two stages.

As shown in Table 2, a D_1 stage brightness response curve was developed for each of the eight $D_0(EO)$ pulps by applying three different levels of ClO_2. The response was characterized, as described earlier,[4] by fitting the data with the following equation:

$$y = b_0 + b_1\left[1 - \exp(-b_2 x)\right] \quad \text{.....(1)}$$

in which y is the brightness of the pulp after the D_2 stage and x is the ClO_2 consumed in the D_2 stage (expressed as $\%ClO_2$, o.d. pulp basis). The usefulness of this model derives not only from the fact that it accurately represents the data, but also from the physical significance that can be attached to the constants. The first, b_0, is the brightness of the pulp entering the stage, and the second, b_1, is the maximum brightness gain that can be achieved in D_2, corresponding to a very high ClO_2 charge. The sum, $b_0 + b_1$, is therefore the brightness ceiling characteristic of a pulp when it is bleached by this sequence with a given ClO_2 charge in D_1. The remaining constant, b_2, is analogous to a reaction rate constant; it characterizes the rate of asymptotic approach to the brightness ceiling as the ClO_2 charge is increased, and is referred to here as the brightness response index. Differentiation of the above equation shows that the rate of brightness increase with respect to increased ClO_2 consumption is the product b_1b_2 when $x=0$. In other words, the initial slope of a plot of brightness versus ClO_2 consumed is b_1b_2.

The left hand portion of Table 3 shows the results of nonlinear regression analysis to fit the above equation to the D_1 brightness data of Table 2, using the $D_0(EO)$ pulp brightness for the y value at $x=0$. It is apparent that the pulps differ with respect to all three parameters in the above equation, showing that bleachability in the $D_0(EO)D_1$ sequence depends on both unbleached kappa number and EA charge. To determine which of the apparent parameter differences are statistically significant, the observed values of each of the parameters, b_0, b_1 and b_2 were subjected to analysis of variance. This allowed the best estimate of each parameter to be obtained for each of the four combinations of EA and unbleached kappa number. This set of best estimates may be viewed as the parameters of a model that consists of four equations of the form of equation (1) and that provides the best predictions of the brightness after the

[4] McDonough, T.J., "Brightness Development in the Final ClO_2 Stages of an ECF Kraft Pulp Bleaching Sequence: Modeling and Effects of Pulping Conditions," 1996 TAPPI Pulping Conference Proceedings, TAPPI Press, Atlanta.

$D_0(EO)D_1$ sequence. The model also serves to summarize the effects of EA and unbleached kappa number on bleachability in this sequence.

Analysis of the b_0 values showed that only the effect of EA is significant, the mean values at low and high EA being 50.6 and 52.8, respectively. Accordingly, these mean values are shown in the right hand portion of Table 3 as parameters of the model. Analysis of the b_1 values showed that only the effect of kappa number is significant, the mean values at low and high kappa number being 34.9 and 31.5, respectively. Analysis of the b_2 values showed that only the effect of kappa number is significant, the mean values at low and high kappa number being 2.40 and 2.75, respectively. These model parameters are also expressed in terms of brightness ceiling and initial slope in the right hand portion of Table 3. The four equations constituting the model are shown graphically in Figure 1, from which it can be seen that increasing EA increases brightness ceiling and decreases the amount of ClO_2 needed for a given brightness, while decreasing the kappa number has a similar effect.

Response in the D_2 Stage

All of the $D_0(EO)D_1$ pulps of Table 2 were bleached by subjecting them to an alkaline extraction stage, followed by another ClO_2 stage (the D_2 stage). Three different ClO_2 charges were used in the D_2 stage, allowing an analysis of D_2 stage response similar to that described above for the D_1 stage. The results are contained in Table 4. For a given charge of ClO_2 in D_1, the b_0 value was higher at lower kappa number and higher alkali charge. The b_1 (brightness gain) value decreased as the D_1 charge (and brightness) was increased, and was higher for high unbleached kappa number pulps. Increasing EA decreased the gain for pulps of low unbleached kappa only. The b_2 value was higher for low EA pulps and for pulps which had been bleached with a higher ClO_2 charge in D_1.

Model parameters for the D_2 stage were obtained by regression analysis of the observed parameters, using the results of an initial analysis of variance to identify the terms to be included in the regression models. This gave the values shown in the right hand portion of Table 4 and allowed effects on the brightness ceiling and initial slope to be delineated. The brightness ceiling of low kappa pulps is unaffected by EA. For high kappa pulps, the brightness ceiling is higher at high EA and is unaffected by increasing the D_1 ClO_2 charge from 0.8 to 1.6%. The initial slope is higher at low EA and high kappa number. As the D_1 charge is increased the initial slope in D_2 first increases, presumably as a result of lower chromophore content, and then decreases, as the entering brightness gets closer to the brightness ceiling.

Full Sequence Model and Analysis of Effects

A full-sequence model was obtained by combining the model parameters of Tables 3 and 4. This allowed prediction of final brightness for any specified combination of unbleached kappa number, EA charge, ClO_2 charge in the D_1 stage and ClO_2 charge in the D_2 stage. Equivalently, the corresponding total ClO_2 requirement to reach a given brightness can be predicted for any of these conditions. Figure 2 shows a series of such predictions for low

kappa, low alkali (LKLA) pulps. It shows predicted brightness for various charges of ClO_2 in D_2 at each of three different charges of ClO_2 in D_1. Since at any given brightness out of D_2 only the lowest total ClO_2 charge is of interest, these are plotted in Figure 3. Figure 4 shows plots of this type for all four combinations of unbleached kappa number and EA. It can be seen that, for high kappa pulps, the brightness ceiling is unaffected by ClO_2 charge in the D_1 stage over the range 0.8-1.6%, and that the high alkali pulps have a higher brightness ceiling. In the case of the low kappa pulps, the brightness ceiling is lower than that for the HKHA pulp and is increased by increasing the ClO_2 charge in the D_1 stage from 0.8 to 1.6%.

Summary and Conclusions

This systematic study has shown that, at a kappa factor of 0.2, final bleaching of southern pine kraft pulp in the later stages of the $D_0(EO)D_1ED_2$ sequence is affected by unbleached kappa number and by the EA charge during pulping, although the effects are smaller after the full sequence than after the D_1 stage. Lower kappa pulps consume more oxidant per unit of kappa number reduction in the first two stages. In the $D_0(EO)D_1$ sequence, increasing EA increases brightness ceiling and decreases the amount of ClO_2 needed for a given brightness, while decreasing the kappa number has a similar effect. When bleaching pulp having an unbleached kappa number of 27 by the $D_0(EO)D_1ED_2$ sequence, the brightness ceiling is unaffected by ClO_2 charge in the D_1 stage over the range 0.8-1.6%, and high alkali pulps have a higher brightness ceiling. This means that for brightness targets of 88 or lower, EA has no effect on total ClO2 requirement, but reaching higher brightnesses is likely to be much more difficult if EA is too low. If the kappa number of high alkali pulps is decreased to 15 by simply cooking for a longer time, the total ClO_2 required in the D_1 and D_2 stages will increase. If the kappa number of low alkali pulps is similarly decreased, the ClO_2 requirement in the D_1 and D_2 stages to reach brightnesses greater than 88 will decrease.

Effects of Sulfidity and Anthraquinone on Bleachability

A study similar to the one described above is underway to assess the effects of sulfide and anthraquinone (AQ) on bleachability. The approach we are using is to prepare laboratory pulps of unbleached kappa number 30 from southern pine chips by soda, soda-AQ, kraft and kraft-AQ processes, and then to bleach each pulp under a variety of conditions of kappa factor, D_1 ClO_2 charge and D_2 ClO_2 charge, allowing the effects of AQ and sulfidity to be assessed. We have made considerable progress towards this goal by identifying pulping conditions, preparing the required pulps and bleaching them with a range of D_1 and D_2 ClO_2 charges, after delignifying in the $D_0(EO)$ partial sequence at 0.2 kappa factor.

Preparation of Pulps

Table 5 shows the pulping conditions and pulp characteristics for the desired pulps as well as for pulps which were obtained en route to finding the correct pulping conditions. Kraft and kraft-AQ pulps of the desired kappa number were readily obtained, and the soda-AQ pulp was obtained after only one trial cook. Finding conditions that would yield 30 kappa soda pulp was more difficult. After completing cooks 5-3 and 5-4, we resorted to a series of microdigester

cooks to find appropriate conditions. The microcook results, shown in Table 6, led to the conditions that produced pulp 5-5 in Table 5.

Response in the $D_0(EO)D_1ED_2$ Sequence

All four pulps have now been bleached by the $D_0(EO)D_1ED_2$ sequence, using a D_0 kappa factor of 0.2, ClO_2 charges in the D_1 stage of 0.8, 1.2 and 1.6%, and ClO_2 charges in the D_2 stage of 0.2, 0.4 and 0.8%. The experimental data are shown in Tables 7 and 8. Additional data was obtained by bleaching samples of the AQ pulps after treatment to remove small metal particles that were observed in the pulp. The data from these experiments, which did not differ significantly from those obtained by bleaching the untreated pulp, are included in Table 9. analysis of the data has not yet been completed, several preliminary conclusions may be drawn. Table 9 contains the results of nonlinear regression analysis of the AQ pulp brightness response curves, done in the same manner as described earlier in this report. It is apparent that the brightness ceiling of the kraft-AQ pulp is 2-3 points higher than that of the soda-AQ pulp and that the brightness ceiling is insensitive to the ClO_2 charge in the D_1 stage over the range 0.8-1.6%. Inspection of the raw data in Table 8 for the corresponding pulps made without AQ leads to the same conclusions and also suggests that AQ slightly decreases the brightness ceiling of the kraft pulp, accentuating the difference between kraft and soda. It thus appears that bleachability is positively affected by sulfidity and negatively by AQ.

Combined Effects of Several Pulping Variables on Bleachability

Experiments are in progress to compare the bleachabilities of pulps of the same kappa number made under two sets of conditions that differ with respect to effective alkali charge, sulfidity, temperature and liquor-to-wood ratio. The conditions were chosen to test the hypothesis that bleachability will be favored by a combination of high sulfidity, high alkali charge, high liquor-to-wood ratio and low temperature, and adversely affected by the opposite combination. Other objectives are to establish the maximum range over which bleachability may be expected to vary for batch kraft pulps, and to provide samples that differ substantially in bleachability for experiments designed to identify pulp characteristics that correlate with bleachability.

Pulps are being prepared at sulfidity 40%, EA charge 30%, temperature 160 deg. C and liquor-to-wood ratio 6:1, and also at sulfidity 5%, EA 14%, temperature 180 deg. C and liquor-to-wood ratio 3:1. Preliminary pulping experiments have been done to determine the required H-factors, and pulp preparation is in progress.

Systematically Varied Pulping Conditions and Bleachability

Work has been initiated to survey the effects of systematically changing kraft pulping variables over wide ranges on the response of the resulting pulp to delignification by oxygen and ClO_2. A response surface experimental design is being used to study the effects of, and interactions between, liquor-to-wood ratio, effective alkali, sulfidity, temperature, alkali profiling, and dissolved solids profiling.

An important initial step is to determine the necessary H-factor at each of the many required combinations of the above-mentioned variables. For that purpose, we are using an empirical pulping model based on unpublished work done several years ago in our laboratory. To account for differences in raw materials and equipment, the model is being updated by carrying out a preliminary response surface experiment in microdigesters. For each combination of values of the pulping variables mentioned above, the model is used to predict the H-factor needed to reach a kappa number of 30. A pulping run is done at this H-factor, the pulp is screened, and its kappa number is determined. The deviation of the actual kappa number from the intended value of 30 is recorded, and the resulting database of deviations is used as the dependent variable in a regression analysis with the pulping variables as independent variables. The resulting relationship can then be combined with the original model to update it.

To date, we have completed 19 microdigester runs, for which the results are shown in Table 10. A preliminary regression analysis containing only significant terms gave an R^2 value of 0.89 and a standard error of estimate of 3.1. The close agreement between the replicate cooks in Table 10 speaks for the quality of the data. The disparity between the standard error and the replicate reproducibility suggests that the regression equation can be substantially improved by modifying the form of the equation to be fitted.

Hexeneuronic Acids and Bleachability

One of the goals of our work on bleachability is to identify one or more pulp characteristics that correlate with bleachability to an extent that will allow them to be used as predictors of bleachability. A list of candidates for such characteristics might include, for example, the content in the residual lignin of structural features such as phenolic hydroxyl groups, condensed aromatic units or interunit ether linkages; unbleached pulp brightness; parameters that define the kinetics of reaction of the pulp with oxidants such as chlorine dioxide or hydrogen peroxide; or measures of the degree of association between lignin and carbohydrate, such as the carbohydrate content of enzymatically liberated lignin.

Another possibility is that the content of hexeneuronic acids (HA) might correlate with bleachability. These oxidizable and acid-hydrolyzable components of the carbohydrate fraction of pulp inflate the kappa number and consume bleaching chemicals. If such groups are more readily oxidized by bleaching chemicals than lignin, pulps with high HA contents might be expected to be more easily bleachable than pulps of the same kappa number with low contents of such groups. Although direct practical application of such knowledge may be limited, the degree to which HA contributes to the kappa number of any given pulp is needed for the correct interpretation of bleachability measurements.

Accordingly, we have carried out a limited amount of experimental work to identify appropriate conditions for measuring HA content and have measured it in low and high effective alkali pulps. Since HA content is measured as the difference between kappa numbers before and after hydrolysis, it was important to find conditions for washing the pulp prior to

analysis that will ensure that the kappa number reduction is due to removal of HA by hydrolysis and not to leaching of residual dissolved lignin. Using a single laboratory-prepared kraft pulp as test material we performed kappa number determinations in quadruplicate after subjecting the pulp to various washing and leaching treatments. The pulp, after washing by routinely used procedures, had nominal kappa number of 25.13 ± 0.09. Washing by 20 successive displacements in a Buchner funnel at a wash liquor ratio of approximately 12:1 had no effect on the kappa number. Leaching with deionized water at 0.33% consistency for 1, 8 and 24 hours reduced it to 24.91, 24.71 and 24.78 respectively. This indicated that a leaching period of 8 hours prior to analysis is necessary and sufficient to ensure accurate determination of HA. This conclusion was corroborated by measurements of filtrate TOC after leaching.

Analysis of a pulp produced with 16% EA gave kappa numbers of 24.63 ± 0.07 before hydrolysis and 22.02 ± 0.09 after hydrolysis, corresponding to an HA content equivalent to 10.6% of the initial kappa number. A similar determination on 22% EA pulp gave an HA content of 5.5% an observation consistent with the apparent lack of effect of EA on ease of removal of lignin in the first two stages of bleaching, as indicated by the data in Table 2.

Elemental Chlorine Free Bleaching

Work on elemental chlorine free (ECF) bleaching with chlorine dioxide under this project is addressing two areas: (1) the use of very short retention times in D_0 stages to provide a low-capital alternative to conventional D_0 bleaching and to decrease AOX formation, and (2) identification of improved operating conditions for ECF sequences.

Short Retention Time D_0 Stages

Laboratory work has demonstrated the feasibility of reducing the duration of the D_0 stage to times in the 1-3 minute range without any substantial detrimental effect on the ability of the full sequence to reach a high final brightness.[3] We have therefore proposed to seek a larger scale trial to confirm the benefits.

To this end, we have begun negotiation with a Georgia producer of bleached kraft pulp to try this technology at the mill. A requirement of the host mill will probably be that we first perform a series of laboratory experiments on the mill's unbleached pulp to demonstrate that the proposed trial has a good chance of success.

Optimizing D_1 Stage pH in ECF Sequences

A systematically designed experimental program is in progress to confirm that the pH dependence of the performance of the D_1 stage is unaffected when all of the Cl_2 in the first stage of a conventional bleach sequence is replaced by ClO_2. Anecdotal evidence from operating mills suggests that this may not be the case.

The experimental design is a full factorial arrangement that incorporates two bleaching sequences [$D_0(EO)D_1$ and $(DC)(EO)D_1$], two levels of stage-to-stage liquor carryover (none and a level of carryover into each stage that is typical of an operating mill) two kappa factor levels, 0.15 and 0.25, three levels of ClO_2 charge in D_1 (0.4, 0.8 and 1.6%) and four exit pH levels (2, 3, 4 and 5). Measurements will include brightness, reversion, dirt count and viscosity. Measurement of dirt removal efficiency will be facilitated by enriching the unbleached pulp in shives. Some or all of the bleach filtrates will be analyzed by ion capillary electrophoresis for chloride, chlorite and chlorate.

Pulp was prepared in the IPST 2 ft.^{3} digester from southern pine chips obtained from a Georgia mill. The conditions used were 16% EA, 25% sulfidity, 170 deg. C, 4:1 liquor-to-wood ratio, H-factor 1650, and the size of the chip charge was 6000 g. o.d. Three cooks were done, giving kappa numbers ranging from 28.1 to 32.3. The three pulps were thoroughly washed, screened, centrifuged and fluffed. They were then blended and re-fluffed to ensure uniformity. The resulting pulp had a kappa number of 30.3. Two additional cooks were done to provide shives for enrichment of the unbleached pulp. These cooks were terminated at kappa number 46. The screen rejects were passed twice through a laboratory 12-inch disc refiner, the first pass being at a disc clearance of 0.030" and the second at 0.010". Bleaching experiments are now in progress.

Chlorine Compound Free Delignification and Bleaching

Research on bleaching without chlorine compounds under this project has included studies of ozone bleaching kinetics, and student work on delignification with oxygen and peroxide. In addition, planning is in progress for work on the effects of delignification with oxygen on pulp properties.

Ozone Bleaching Kinetics

A semibatch flow reactor (the same one used in studies that were reported in earlier PAC reports) was used to study the ozonation of softwood kraft pulp before and after oxygen delignification. For comparison, the same pulp was ozonated after delignification in a DED sequence. The objectives were to determine the stoichiometry of the ozonation reaction, and to obtain rate-concentration relationships that will be used in formulating a general rate law.

Unbleached southern pine, after classification to remove fines and chelation with EDTA, was exposed to a flowing pH 3.5 buffer solution containing 4 mg ozone per liter. The pulp (7.2 g. o.d.) was added to a well mixed 1.8 L vessel through which the solution passed at a constant 150 mL/min. The pulp was prevented from leaving the vessel by a fine-mesh screen at the outlet. As observed in previous experiments, contact with the pulp caused an immediate sharp decrease in the ozone concentration, to 1 mg/L. Even though the ozone in the vessel was continuously replenished by fresh 4 mg/L solution flowing into it, the concentration at the outlet remained low, as a consequence of the continued consumption of ozone by the pulp.

A mass balance around the vessel allowed determination of the total amount of ozone consumed, and measurement of the kappa number of the ozonated pulp gave the amount of lignin removed. This allowed the stoichiometry of the reaction to be determined for reactions of varied duration. The ozone consumption was directly proportional to kappa number reduction, showing that the stoichiometry is constant over the range of delignification extents studied (0-28%). The slope of the line was 0.13 g ozone consumed per g lignin removed. (The corresponding figure for chlorine dioxide followed by caustic extraction is 0.61!) This value is required to derive a rate law from the ozone reaction kinetics database we have previously developed in this reactor system.

The current experiments also demonstrated that, for southern pine kraft brownstock the kappa number reduction increases linearly with time over the range studied. The reaction may therefor be of zero order in lignin – the rate of delignification does not decrease as the concentration of remaining lignin decreases. This suggests that oxidation of fiber wall lignin by ozone is a "surface" reaction.

Another piece of information needed for full interpretation of the kinetics is the split between ozone consumed by lignin and ozone consumed by carbohydrate. To derive information on this parameter, a sample of the unbleached pulp was delignified in a DED sequence and the fully bleached pulp was ozonated as described above. It consumed a substantial amount of ozone, approximately 0.25 mg/min versus 0.45 mg/min for the unbleached pulp. Although the DED bleached pulp was not completely free of lignin (kappa no. 2.6) it is clear that the rate law for ozone disappearance will necessarily have both a term for reaction with lignin and a term for reaction with carbohydrate.

Experiments were also conducted in which the same kraft pulp was oxygen delignified, from kappa no. 26.7 to kappa no. 16.3, before ozonation. The effect of the oxygen predelignification on the ozonation kinetics was quite pronounced. The rate of delignification by ozone was increased, and the reaction was no longer zero order in lignin – the rate of lignin removal decreased as delignification progressed. Since ozone is unlikely to be used commercially without a prior oxygen delignification stage, further experimentation will emphasize the behavior of oxygen delignified pulps.

Much has been learned about ozone delignification kinetics from work to date on this project, but, due to the complexities of the system and the inherent difficulty of the experiments, a rate law has yet to be obtained. Nevertheless, we feel that the semibatch reactor system employed is uniquely well-suited to the study of this rapid reaction and that we now have the necessary know-how to make good progress. Furthermore, data on the kinetics of ozone delignification are needed, both to improve selectivity and to enable the design of improved ozonation reactors. Both are timely objectives given the growing recognition of ozone's capabilities as a delignification agent in both ECF and TCF sequences. Accordingly, further experiments are

planned. Pulp which has been delignified by oxygen to varying degrees will be ozonated in the semibatch reactor after removal of fines and chelation. For each pulp, experiments will be conducted at different consistencies and ozone concentrations. A simulation program will be developed to predict outlet concentration behavior for an assumed rate law under given operating conditions, and thus to allow rate laws to be inferred from outlet concentration behavior.

Oxygen-Peroxide Delignification

An extensive response surface study of delignification with combinations of O_2, NaOH, H_2O_2, $MgSO_4$, cyanamide (H_2NCN), and DTMPA has been completed by an M.S. student, Ms. T. Kubicar. The raw material was repulped old corrugated containers (OCC) having a kappa number of approximately 100. The objective was to optimize the charges of the components of the bleach liquor, to minimize the chemical cost to reach any specified kappa number. The study showed that neither cyanamide nor DTMPA were cost effective. Delignification to kappa number 42 was optimally achieved by applying 7% NaOH, 0.8% $MgSO_4$ and 1.2% H_2O_2. Use of these conditions in an AODODED sequence gave a brightness of 83 with a total ClO_2 charge of 3%. A control experiment in which the DEDED sequence was used gave a brightness of only 76 with a total ClO_2 charge of 8.5%. The viscosity of the AODODED pulp was lower than that of the control pulp, but the zero-span tensile indices of the two pulps were similar.

Extended Delignification Through Oxygen Treatment (Storker Moe, A. Ragauskas)

In recent years there has been an increased focus on the adverse environmental effects of effluents released from pulp mills. The minimum-impact mill has, today, become a goal for many pulp manufacturers. Different technologies are being investigated in order to minimize pulp mill pollution, but perhaps the most common solution to minimize environmental impact has been low-kappa pulping (kappa number range 20-25) followed by oxygen delignification to kappa numbers between 10 and 15 and post-oxygen ECF or TCF bleaching sequences.

Another approach which has been mentioned in the literature, is high-kappa pulping followed by extended oxygen delignification. Although not commonly known in the international community, this approach has – albeit for other reasons – been used in the Peterson Moss mill in Moss, Norway. The main product of this mill is unbleached linerboard for corrugated cartons, but for several years about 20% of the mill's pulp production was sold to another mill for grease-proof paper production. The Moss mill uses a polysulfide/anthraquinone white liquor, pulping Scandinavian softwood (a mix of Norway spruce and pine) to kappa numbers between 60 and 70. The market pulp was then subjected to a two-stage oxygen/alkali delignification resulting in 66% kappa number reduction and pulp properties comparable to a one-stage oxygen/alkali treatment for a 50% kappa number reduction. This pulp (kappa number ~22) was then bleached using a C(EOP)HP sequence to 85% ISO brightness. Extended digester delignification has some obvious disadvantages, namely decreased pulp

strength (which has mostly been overcome though new pulping technologies, e.g. ITC continuous pulping, or Superbatch batch pulping) and lower yields, due to the poor selectivity of the pulping chemicals in the final phase.

On the other hand, the reason for the strongly increased popularity of oxygen delignification is the improved selectivity of oxygen over pulping chemicals at lower kappa numbers. Extended oxygen delignification would, therefore, seem a very interesting alternative to extended cooking. By pulping to higher yields (and kappa numbers), one would expect to retain more of the carbohydrates, especially the hemicelluloses, in the pulp. This could then result in higher yields, lower recovery loads and possibly a pulp with increased interfiber bonding properties due to a somewhat higher hemicellulose content. This principle is especially interesting in view of recent advances in chemical activation of pulps between oxygen steps, using peracids or ozone.[5]

Project overview

Phase 1

Aim

To characterize structural properties of residual lignins from both unbleached and oxygen delignified pulps of various kappa numbers, and of dissolved lignins and carbohydrates from the oxygen delignification of these pulps. The structural properties of the residual lignins will be correlated to the bleachability of the pulps.

Status

A range of pulps have been prepared in a CRS flow-through laboratory digester. The raw material was pure Norway spruce (*Picea abies*) chips. The pulping conditions for two of the pulps were chosen to approach pulping conditions used in actual mills (the Peterson Moss mill in Moss, Norway and the Norske Skog Tofte mill in Tofte, Norway were used as examples). The pulps are listed in Table 11.

These pulps have then been oxygen delignified to approximately 50% kappa numbers, the PS/AQ high-yield kraft pulp also through a two-stage oxygen delignification to 65% kappa number decrease. Residual lignins have been isolated from the unbleached and the oxygen delignified pulps, dissolved lignins have been isolated from the delignification effluents and the black liquors, and dissolved carbohydrates have been isolated from the effluents.

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[5] Li, X.-L., Fuhrmann, A. & Rautonen, R. (1995): "Optimization and activation of two-stage oxygen delignification", SCAN report no. 658, KCL, Finland

Analyses

- Residual and dissolved lignin structural characterization by ^{1}H-NMR, ^{31}P-NMR and/or ^{13}C-NMR.
- Monosaccharide composition of dissolved carbohydrates according to TAPPI test method.
- Carboxylic acid content of pulps.
- Bleachability (kappa number decrease after D_0E) of oxygen pulps.

Phase 2

Aim

To investigate the bleachability of high-yield kraft pulp after an OxO bleach sequence, using ITC and conventional kraft pulps after a single-stage oxygen delignification as references.

Table 11: Pulps prepared for the investigation

Kappa no.	Pulping conditions	White liquor characteristics
45.4	Conventional continuous, PS/AQ WL	102.08 g/l effective alkali (as NaOH) 22.29% sulfidity 4.5±0.5 g/l polysulfide AQ charge: 0.05% (on wood)
~30	ITC™ simulation with BL impregnation	123.84 g/l effective alkali (as NaOH) 38.92% sulfidity
23.3	Conventional continuous	123.84 g/l effective alkali (as NaOH) 38.92% sulfidity
22.4	ITC™ simulation	123.84 g/l effective alkali (as NaOH) 38.92% sulfidity
18.3	ITC™ simulation	123.84 g/l effective alkali (as NaOH) 38.92% sulfidity

Residual (and possibly dissolved) lignins after the Ox and the OxO sequences will be characterized and correlated to the bleachability of the pulps in a $D_0(EOP)D_1$ sequence.

Planned work

The high-yield pulp will be bleached OPaaO $D_0(EOP)D_1$. The two medium-to-low kappa number pulps will be bleached $OD_0(EOP)D_1$ and used for reference. Residual and possibly dissolved lignins will be isolated after the OPaa and the OPaaO sequences and structural characteristics of the residual lignins will be correlated to the bleachability of the pulps, taken as chlorine dioxide charge (in D_1) required to reach 90% ISO brightness. The bleached pulps will be characterized with respect to carbohydrate composition (i.e. hemicellulose content), viscosity and papermaking properties.

Delignification and Pulp Properties

A meeting of representatives of the Pulping and Bleaching, Wood Chemistry and Paper Physics Groups was held to construct a proposal for collaboration among these groups to

achieve the goal of the present project that concerns the effect of delignification on pulp properties. The result was a proposal to investigate the effects of lignin removal by extended kraft pulping, oxygen, chlorine dioxide and chlorine on refinability and intrinsic fiber properties. This proposal will be discussed with both the Chemical Pulping and Paper Physics Project Advisory Committees during the week of March 24, 1997.

Measurement of Anthraquinone Concentration in Pulping Liquors

Anthraquinone has become a commonly used pulping additive because it improves yield and accelerates delignification. Mills have found many ways to capitalize on the benefits of using AQ over the past two decades. Now, given the industry's growing committment to extended delignification and low-impact bleaching, mills have even more incentive to take full advantage of AQ's benefits.

In an effort to optimize the performance of AQ, researchers want to study the effects of controlling its concentration during pulping. Such a control capability does not presently exist, however, because measurements of AQ concentration in pulps or liquors simply cannot be performed fast enough. The objective of this work was to identify a method that would be rapid enough to measure pulping liquor AQ concentration in an at-line or, preferably, on-line capacity.

Two spectroscopic techniques were studied: near-infrared (NIR) and fluorescence. We concluded that neither of these methods were viable for the direct determination of AQ in weak black liquor samples. The NIR method suffered from sensitivity limitations and the fluorescence method was compromised by strong interfering fluorescence caused by liquor components other than AQ.

Alternatively, by extracting the AQ from liquor samples with chloroform, and analyzing the fluorescence of the extracts, it was possible to demonstrate several interesting correlations between the observed fluorescence and an independently determined AQ concentration. This, however, did not lead to the conclusion that fluorescence was a good indicator of AQ concentration in liquor extracts. The results instead were more consistent with the possibility that the fluorescence observations reflected the formation of an unidentified AQ reaction by-product.

The speed of spectroscopy made it a suitable candidate for this study. But, unfortunately, the spectroscopic methods do not appear to be specific enough to detect low concentrations of AQ in liquors and extracts that have highly complex chemical compositions. Hence, we concluded that the extraction/spectroscopy approach to *directly* measuring AQ in liquors was not likely to succeed because of the encountered drawbacks and complexities associated with it. However, further work with the extraction/spectroscopy approach may lead to identification of the AQ reaction by-product and may show whether its measurement could serve as an indirect indicator of AQ concentration. In addition, AQ profiling could

be done to study its effect on the formation of the by-product and on the final quality of the pulp, in order to determine if the by-product can serve as a marker for pulp properties development.

An alternative recommendation is to adopt existing chromatographic separation techniques that have demonstrated good specificity to AQ. At least two such methods exhibit the potential to be optimized and made fast enough for this type of application.

Table 1: Low- and High-Kappa Pulps Made with Different Alkali Charges

Pulp Type	Eff. Alk., % o.d.w.	H-Factor	Repli-cate No.	Kappa Number	Visc., mPa.s	Bright-ness
Low Kappa, Low Alkali (LKLA)	16	4000	1	15.7	17.8	26.5
			2	15.5	15.7	30.7
Low Kappa, High Alkali (LKHA)	22	2100	1	15.6	15.0	29.5
			2	14.6		34.5
High Kappa, Low Alkali (HKLA)	16	1569	1	26.3	34.6	30.0
			2	26.3	35.0	28.7
High Kappa, High Alkali (HKHA)	22	763	1	26.8	29.5	31.1
			2	28.3	31.7	31.2

Table 2: D(EO)D Bleaching of High- and Low-Kappa Pulps Made with Different Alkali Charges

Unbl. Pulp	D_0(EO) Stages			D_1 Stage			
	Kappa Number	Active Cl per Unit Kappa Reduction	Bright-ness	ClO_2 Charge, % o.d.p	Exit pH	ClO_2 Cons., % o.d.p	Bright-ness
LKLA-1	3.9	0.266	48.2	0.8	3.5	0.78	79.4
				1.2	3.8	1.10	82.1
				1.6	3.7	1.33	84.6
LKLA-2	3.0	0.248	52.4	0.8	4.0	0.70	80.6
				1.2	4.0	1.03	82.7
				1.6	3.9	1.25	84.9
LKHA-1	3.7	0.262	51.6	0.8	4.0	0.79	80.2
				1.2	3.7	1.16	83.9
				1.6	3.4	1.39	85.2
LKHA-2	3.6	0.265	53.4	0.8	3.5	0.78	82.4
				1.2	3.6	1.14	83.2
				1.6	3.9	1.29	85.8
HKLA-1	3.6	0.232	51.1	0.8	4.0	0.80	79.4
				1.2	3.7	1.16	80.6
				1.6	3.5	1.45	82.2
HKLA-2	4.4	0.240	50.6	0.8	3.8	0.80	80.2
				1.2	3.9	1.14	81.6
				1.6	3.8	1.53	83.0
HKHA-1	4.0	0.235	52.6	0.8	4.7	0.80	78.5
				1.2	4.4	1.02	81.3
				1.6	4.0	1.34	81.7
HKHA-2	4.3	0.236	53.7	0.8	4.6	0.75	80.7
				1.2	4.3	0.97	83.7
				1.6	4.5	1.23	83.7

Table 3: D1 Stage Response Parameters

Pulp Type	Experimental Values			Model Values				
	Entering Brightness, b_0	Brightness Gain, b_1	Brightness Response Index, b_2	Entering Brightness, b_0	Brightness Gain, b_1	Brightness Response Index, b_2	D_1 Bright-ness Ceiling, b_0+b_1	Initial Slope, b_1b_2
LKLA	48.2 52.4	38.3 33.3	2.12 2.62	50.6	34.9	2.40	85.5	84
LKHA	51.6 53.4	35.6 32.3	2.05 2.82	52.8	34.9	2.40	87.7	84
HKLA	51.1 50.6	31.2 32.5	2.91 2.95	50.6	31.5	2.75	82.1	87
HKHA	52.6 53.7	30.6 31.6	2.45 2.69	52.8	31.5	2.75	84.3	87

Table 4: D2 Stage Response Parameters

Unbl. Pulp	ClO_2 in D_1, % o.d.p.	Experimental Values: Entering Brightness, b_0	Experimental Values: Brightness Gain, b_1	Experimental Values: Brightness Response Index, b_2	Model Values: Entering Brightness, b_0	Model Values: Brightness Gain, b_1	Model Values: Brightness Response Index, b_2	Model Values: D_1 Brightness Ceiling, b_0+b_1	Model Values: Initial Slope, b_1b_2
LKLA	0.8	79.4	8.8	9.48	80.3	8.2	11.70	88.5	96
	0.8	80.6	9.0	7.95					
	1.2	82.1	7.0	13.75	82.5	6.7	24.30	89.3	164
	1.2	82.7	7.0	26.22					
	1.6	84.6	4.7	20.00	84.8	5.3	16.40	90.0	86
	1.6	84.9	4.7	25.53					
LKHA	0.8	80.2	7.6	7.90	81.1	7.3	6.00	88.4	44
	0.8	82.4	6.3	6.82					
	1.2	83.9	4.6	15.03	83.3	5.9	9.10	89.1	53
	1.2	83.2	6.4	7.55					
	1.6	85.2	4.2	12.84	85.5	4.4	10.60	89.9	47
	1.6	85.7	5.3	6.72					
HKLA	0.8	79.4	8.8	16.49	79.5	8.9	16.40	88.4	146
	0.8	80.2	8.7	11.74					
	1.2	80.6	7.7	19.98	81.0	7.4	24.30	88.4	180
	1.2	81.6	7.3	37.30					
	1.6	82.2	6.4	11.14	82.5	5.9	11.70	88.4	69
	1.6	83.0	6.3	9.83					
HKHA	0.8	78.5	11.3	6.27	80.3	9.8	10.60	90.0	103
	0.8	80.7	8.8	8.45					
	1.2	81.3	8.6	6.06	81.8	8.3	9.10	90.0	75
	1.2	83.7	6.1	7.67					
	1.6	81.7	7.6	10.07	83.2	6.8	6.00	90.0	41
	1.6	83.7	6.5	7.38					

Table 5: Preparation of Pulps for Comparative Bleachability Study

Pulp Sample No.	Process	Effective Alkali, % o.d. wood	Time at 170°C, min.	H-Factor	Kappa Number	Viscosity, mPa.s	Brightness	Notebook Reference
5-1	Kraft	16	90	1600	31.2	31.1		4286-102
5-2	Kraft-AQ	16	70	1300	29.6	27.1	27.6	4286-103
5-3	Soda	16	242	4000	85.0			4286-104
5-4	Soda	16	510	8100	83.4			4286-105
5-5	Soda	20	330	5220	32.8	9.3		4286-119
5-6	Soda-AQ	16	180	3000	51.5			4286-106
5-7	Soda-AQ	16	260	4250	29.0	15.5	26.1	4286-106

Notes: 1. Sulfidity, where applicable, was 25% of active alkali.
2. Anthraquinone (AQ), when present, was charged at 0.1% of o.d. wood weight.
3. Temperature raised from 100°C to 170°C in 85-95 min.
4. Chips were never-dried southern pine from a coastal U.S. mill.
5. Liquor-to wood ratio was 4:1.
6. Pulps prepared from 6000 o.d. g chips in 2 $ft.^3$ digester.

Table 6: Exploratory Microdigester Soda Cooks

Pulp Sample No.	Effective Alkali, % o.d. wood	Time at 170°C, min.	H-Factor	Kappa Number	Yield, % o.d. wood	Notebook Reference
6-1	20	360	6000	25.7	33.7	4286-118
6-2	24	360	6000	16.6	33.7	4286-118
6-3	28	360	6000	13.8	30.3	4286-118
6-4	20	480	8000	18.8	35.0	4286-118
6-5	24	490	8000	13.5	31.1	4286-118
6-6	28	480	8000	11.0	27.2	4286-118

Notes: 1. Cooks of 50 o.d. g wood in 500 mL microdigesters
2. Temperature raised from 80°C to 170°C in 90 min,
3. Chips were never-dried southern pine from a coastal U.S. mill
4. Liquor-to wood ratio was 4:1

Table 10: Microdigester Cooks to Update Pulping Model

L/W Ratio	EA, %	Sulfidity, %	Temp., Deg. C	Time, min.	H-Factor	Predicted Kappa No.	Actual Kappa No.
3.25	18.1	27.5	170	62	1105	31.5	28.1
6.00	24.1	27.4	170	85	1460	29.7	19.4
6.00	18.2	39.7	170	110	1840	29.4	20.5
6.00	18.1	27.4	170	127	2100	34.8	21.7
6.00	18.1	27.4	170	144	2360	29.6	20.7
6.00	18.1	27.4	170	144	2360	29.6	22.2
6.00	18.1	27.4	170	144	2360	29.6	20.1
6.00	12.0	27.5	170	245	3900	30.9	48.3
6.00	18.0	5.0	170	237	3775	30.5	32.7
6.00	18.0	27.5	170	165	2675	25.2	20.0
6.00	18.0	27.5	170	144	2360	29.9	19.6
6.00	18.0	27.5	170	144	2360	29.9	19.8
6.00	18.0	27.5	170	144	2360	29.9	20.6
6.00	18.0	27.5	160	329	2225	30.3	22.0
6.00	18.0	27.5	180	62	2450	30.1	19.8
8.75	18.0	27.5	170	189	3050	30.1	29.1
6.00	12.0	27.5	170	254	4050	30.1	44.3
6.00	18.0	27.5	170	144	2360	29.9	21.6
6.00	18.0	27.5	170	144	2360	29.9	21.9

Table 8. Bleachability of Kraft and Soda Southern Pine Kraft Pulps

Stage	ClO2,%	NaOH,%	Final pH		Res.CLO2,%(as apply)		Kappa #		Brightness	
			Kraft	Soda	Kraft	Soda	Kraft	Soda	Kraft	Soda
							31.2	32.8		
Do	KF=0.2	0	1.60	1.65	trace	trace				
(EO)	60psi O2	2.8	11.85	11.85			3.64	4.24		
D1	0.8	0.4/0.35	5.00	4.55	21.3	10.6			-	82.04
	1.2	0.6	4.55	4.80	15.2	18.2			-	83
	1.6	0.8/0.75	4.70	4.20	18.2	15.2			-	84.6
E-0.8		0.5	11.50	11.50					81.8	77.8
E-1.2		0.5	11.55	11.50					84.4	78.0
E-1.6		0.5	11.60	11.50					85.1	81.5
D-0.8	0.0	0	-	4.30					-	78.7
	0.2	0.005	4.55	4.60	6.1	6.1			89.1	85
	0.4	0.15/0.10	4.90	4.50	15.2	6.1			89.8	87.1
	0.8	0.20	4.10	3.70	30.4	13.7			90.5	87.9
D-1.2	0.0	0	-	4.05						78.8
	0.2	0	3.70	4.50	6.1	6.1			90.4	86.9
	0.4	0.10	4.15	4.10	15.2	4.6			90.9	87.6
	0.8	0.20/0.25	4.10	4.00	28.9	10.6			91.1	87.9
D-1.6	0.0	0	-	4.35						82.8
	0.2	0	4.15	4.50	6.1	6.1			90.9	88.4
	0.4	0.10	4.65	4.40	21.2	9.1			91.3	88.7
	0.8	0.20	4.25	4.35	27.3	13.7			91.3	88.74

Table 7. Bleachability of Kraft-AQ and Soda-AQ Southern Pine Kraft Pulps

Stage	ClO2,%	NaOH,%	Final pH		Res.CLO2,%.(as apply.)		Brightness	
			K.-AQ	S.-AQ	K.-AQ	S.-AQ	K.-AQ	S.-AQ
Do	KF=0.2	0	1.60	1.65	0			
(EO)	60psi O2	2.8	11.85	11.65				
D1	0.8	0.4	4.3	4.5	8.0	6.0		
	1.2	0.6	3.96	4.0	13.2	12.2		
	1.6	0.8	4.5	4.05	18.2	17.5		
E-0.8		0.5	11.7	11.75			82.2	77.4
E-1.2		0.5	11.8	11.7			84	78.9
E-1.6		0.5	11.7	11.7			84.6	79.8
D-0.8	0.2	0	3.7	4.14	12.0	-	88.9	85.1
	0.4	0.1	3.7	3.4	24.3	6.1	89.6	86.9
	0.8	0.15	3.4	3.06	41.0	29.0	90.04	87.5
D-1.2	0.2	0	3.8	4.05	12.15	3.5	89.7	86.9
	0.4	0.1	3.9	3.65	30.4	12.2	90.4	87.55
	0.8	0.15	3.6	3.1	39.5	29.0	90.5	87.8
D-1.6	0.2	0	3.75	4.0	12.15	6.1	90.3	87.5
	0.4	0.1	3.8	3.6	27.3	18.2	90.6	88.2
	0.8	0.15	3.5	3.25	42.5	36.5	90.7	88.4

Table 9: Comparison of Bleachabilities of Kraft-AQ and Soda-AQ Pulps

Unbleached Pulp				D_0(EO) Stages			D_1E_2 Stages				D_2 Stage						
Pulp Type	Kappa Number	Visc., mPa.s	Bright-ness	Kappa Number	Active Cl per Unit Kappa Reduction	Visc., mPa.s	ClO_2 Charge, % o.d.p	ClO_2 Cons., % o.d.p	Bright-ness after D_1	Bright-ness after E_2	ClO_2 Charge, % o.d.p	ClO_2 Cons., % o.d.p	Bright-ness	Bright-ness Ceiling	Initial Slope	Pulp Sample ID No.	Notebk. Ref.
Kraft-AQ	29.6	27.1	27.6				0.8	0.74			0.2	0.18	88.9	90.2	ND	9-1	4286-110
											0.4	0.30	89.6			9-2	4286-110
											0.8	0.47	90.0			9-3	4286-110
							1.2	1.04			0.2	0.18	89.7	90.5	ND	9-4	4286-110
											0.4	0.28	90.4			9-5	4286-110
											0.8	0.48	90.5			9-6	4286-110
							1.6	1.31			0.2	0.18	90.3	90.7	ND	9-7	4286-110
											0.4	0.29	90.6			9-8	4286-110
											0.8	0.46	90.7			9-9	4286-110
Soda-AQ	29.0	15.5	26.1				0.8	0.75			0.2	0.20	85.1	87.8	ND	9-10	4286-113
											0.4	0.38	86.9			9-11	4286-113
											0.8	0.57	87.5			9-12	4286-113
							1.2	1.05			0.2	0.19	86.9	87.8	ND	9-13	4286-113
											0.4	0.35	87.6			9-14	4286-113
											0.8	0.57	87.8			9-15	4286-113
							1.6	1.32			0.2	0.19	87.5	88.4	ND	9-16	4286-113
											0.4	0.33	88.2			9-17	4286-113
											0.8	0.51	88.4			9-18	4286-113
												0	86.7				
De-metaled Kraft-AQ	29.0			3.50	0.227	27.6	0.8	0.78	86.7	83.0	0.2	0.17	90.1	90.6	47	9-19	4286-115
											0.4	0.30	90.6			9-20	4286-115
											0.8	0.52	90.6			9-21	4286-115
												0.00	78.5				
De-metaled Soda-AQ	28.5			4.46	0.232	14.8	0.8	0.78	78.5	76.2	0.2	0.19	85.6	87.7	71	9-22	4286-115
											0.4	0.36	87.1			9-23	4286-115
											0.8	0.58	87.6			9-24	4286-115

Notes: 1. D_0 stage: kappa factor 0.20, 30 min., 45°C, 10% cons'y., exit pH 1.6, trace residual

2. (EO) stage: 2.8% NaOH, 60 psig. O_2, 60 min., 70°C, 10% cons'y., exit pH 11.6-11.9

3. D_1 stage: 180 min., 70°C, 10% cons'y., exit pH 4.2±0.3

4. E_2 stage: 0.5% NaOH, 90 min., 70°C, 10% cons'y., exit pH 12.1-12.2

5. D_2 stage: 180 min., 70°C, 10% cons'y.

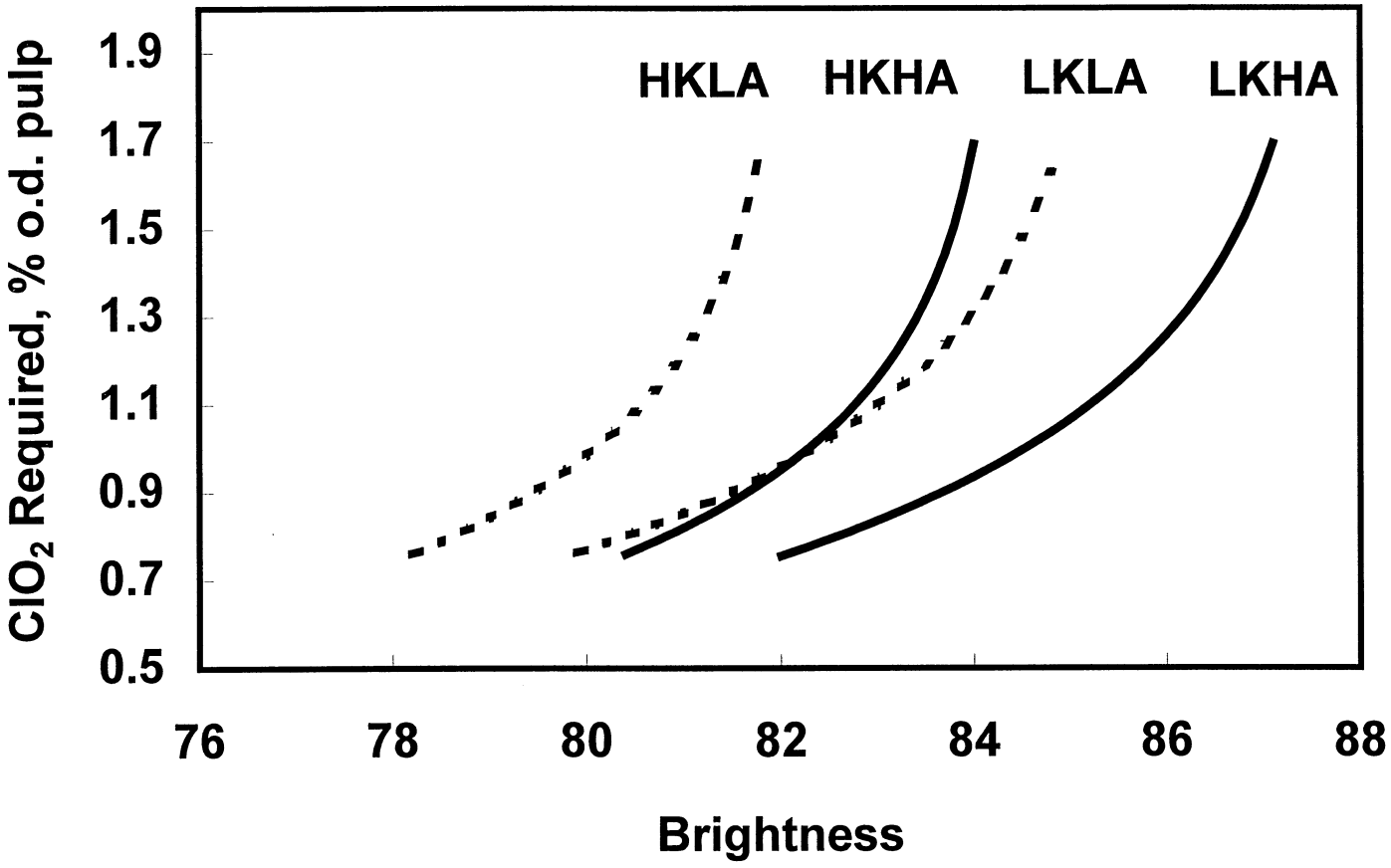


Figure 1. Effects of kappa no. (LK=15, HK=27) and EA charge (LA=16%, HA=22%) on ClO_2 consumption required to reach a given brightness, as given by the model fitted to the experimental data.

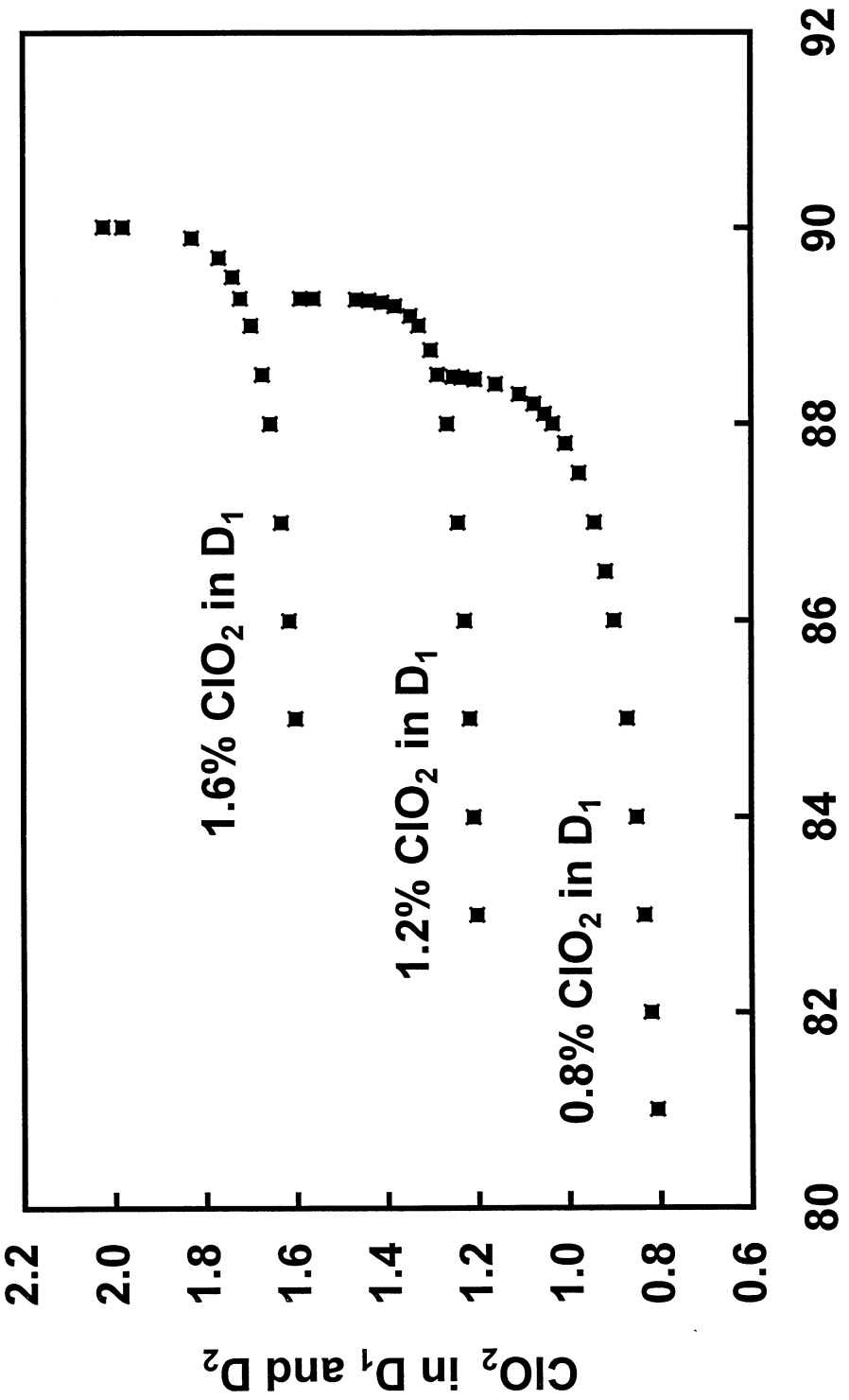


Figure 2. Predicted total ClO_2 requirement in D_1 and D_2 vs. final brightness for LKLA pulp

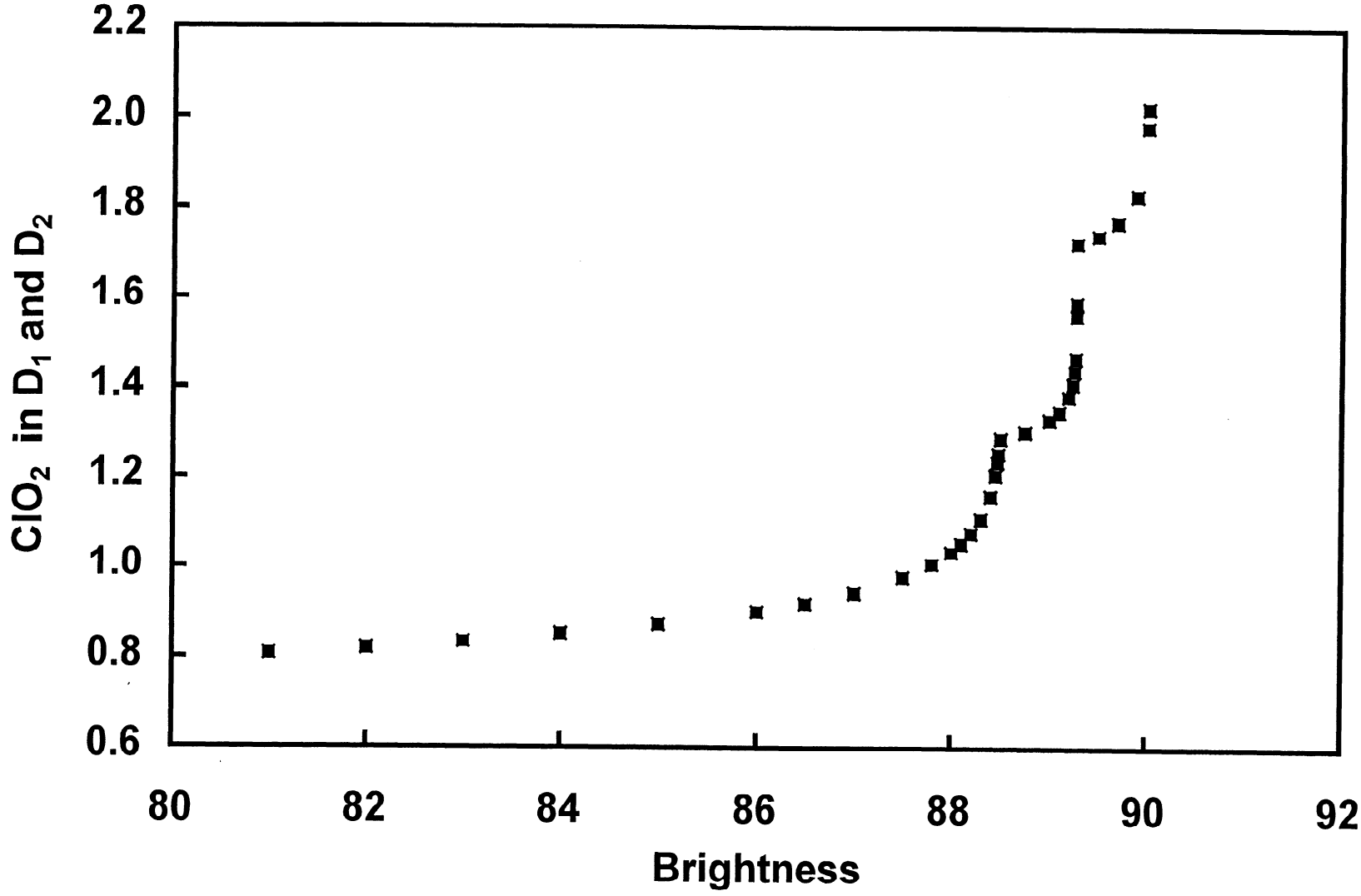


Figure 3. Lowest predicted total ClO_2 requirement in D_1 and D_2 vs. final brightness for LKLA pulp

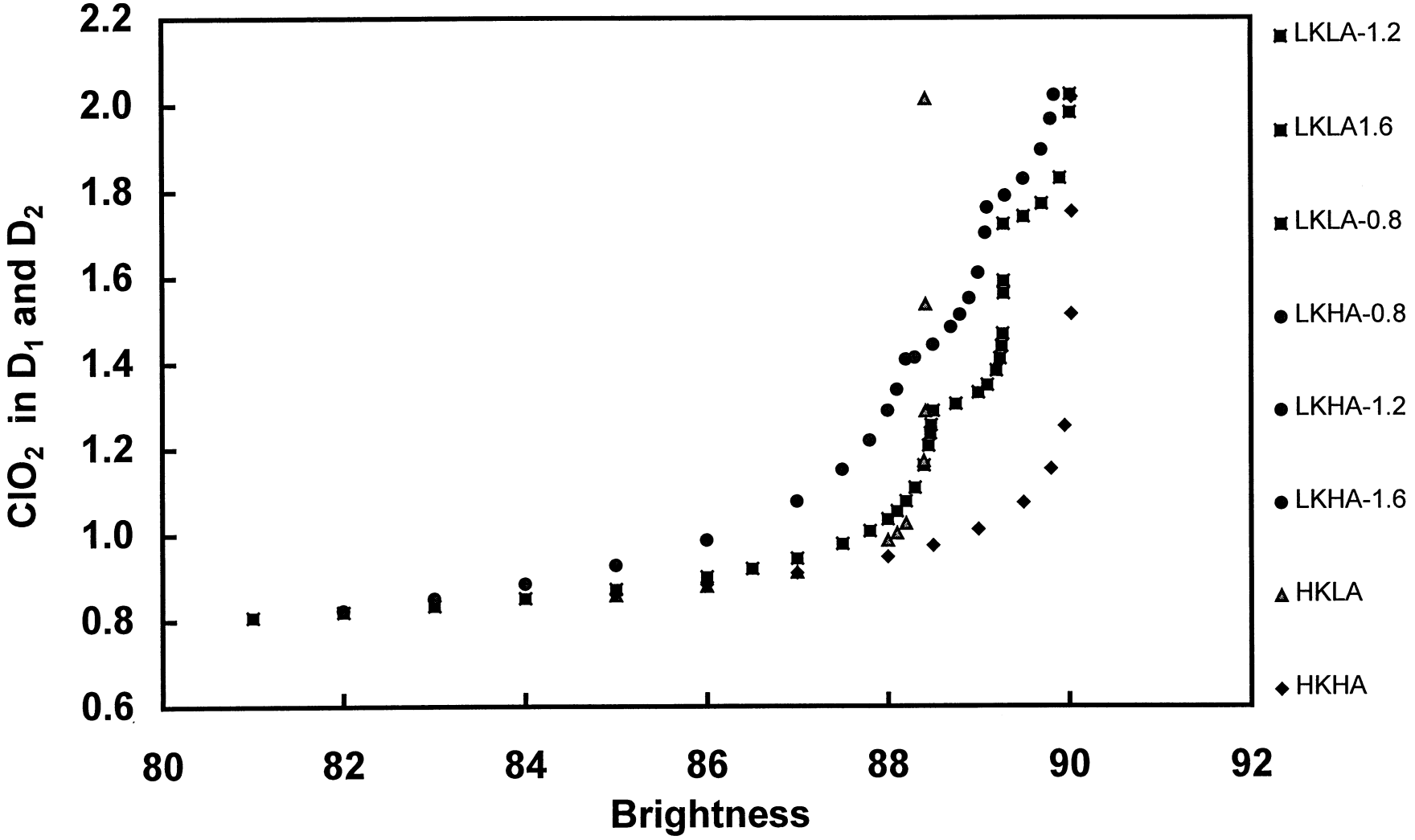


Figure 4. Lowest predicted total ClO2 requirement in D_1 and D_2 vs. final brightness for all four pulp types. Legend indicates pulp type and ClO_2 charge in D_1.

Fundamentals of Bleaching Chemistry

PROJECT SUMMARY

PROJECT TITLE: FUNDAMENTALS OF BLEACHING CHEMISTRY

PROJECT STAFF: D. Dimmel, A.J. Ragauskas, new faculty
L. Allison, E. Althen

FY 97 BUDGET: $270,000

DIVISION: Chemical and Biological Sciences

PROJECT NUMBER: F015

OBJECTIVE:

Provide a fundamental understanding of the physical and chemical reactions that control lignin and carbohydrate degradation during new bleaching sequences. Understand the reasons for selectivity of reactions that occur in selected pulping and bleaching sequences. Work in concert with Project F013 on bleach process technology. Focus areas are ozone bleaching technologies, high efficiency peroxide bleaching, hexenuronic acids, and biobleaching technologies.

GOAL: Improve bleaching processes.

PROGRAM SUMMARY:

Research activities in ozone, peroxide bleaching, hexenuronic acid, and laccase have been accomplished this past fiscal year in project F015.

Ozone

The ozone component of this project is currently being conducted under USDA-sponsored Project 4168, "Improved Selectivity in Ozone Bleaching." The work in this area will be expanded into F015 as time and personnel become available. A membership report is being prepared on past ozone studies; it is expected to be ready for distribution at the Spring PAC meeting.

High Efficiency Peroxide Bleaching - *Art J. Ragauskas*

The long term goal of this project is to develop improved methods of using hydrogen peroxide for conventional and pressurized bleaching conditions. Our research thrust is to define how hydrogen peroxide reacts with lignin, to allow the rational design of new peroxide bleaching technologies.

Current Results: Research efforts over this past fiscal year have accomplished the five research goals established in the spring 1995 PAC including:

1. Determine residual lignin structure after bleaching pulp with P*.

   Accomplishment: P* bleached softwood kraft pulp with a 2, 3, and 4% charge of H_2O_2. Physical properties of the pulp were determined and residual lignin was isolated. Lignin was characterized in terms of functional groups including: acids, formyl units, condensed & non-condensed phenoxy groups, aliphatic, methoxy and aromatic structures.

2. Determine residual lignin structure after bleaching oxygen delignified kraft pulp with P*.

   Accomplishment: P* bleached an oxygen delignified softwood kraft pulp employing 1, 2, and 3% H_2O_2. Physical properties of bleach pulp were determined and residual lignin was isolated and structural features were established.

3. Examine nature of residual lignin after Do(EOP).

   Accomplishment : A softwood kraft pulp was bleached with ClO_2 (0.21 kf) followed by (EOP). Changes in residual lignin structure before and after the Do(EOP) treatment were determined.

4. Determine pH profile for P* at pH less than 7.0

   Accomplishment : Delignification properties of H_2O_2 (2% charge) at 110°C with a starting pH of 10.7, 5.0, 4.5, 4.0, and 3.5 were studied with a southern softwood kraft pulp. Delignification was accompanied with significant loss in viscosity.

5. Examine peroxide reactivity with quinone enriched pulp.

   Accomplishment : A softwood kraft pulp was chemically enriched in ortho-quinones and this resulted in improved peroxide delignification.

Influence of Hexenuronic Acids on Bleaching - *A.J. Ragauskas*

The research goal of this sub-project is to determine what extent hexenuronic acids influence modern North American pulping and bleaching operations. For those operations that are effected by hexenuronic acids, new technologies will be developed to minimize their effects.

Current Results: Research efforts over this past fiscal year have accomplished the three research goals established in the spring 1995 PAC, including:

1. Examine the contribution of hexenuronic acids toward the kappa number of softwood and hardwood kraft pulps.

   Accomplishment : An exploratory studied examined 14 kraft pulps from various North American sources and established that approximately 50% of the hardwood kappa number originated from hexenuronic acids.

2. Develop an experimental method to directly quantify hexenuronic acids in pulp.

   Accomplishment : Literature methods were followed to measure the concentration of furoic acid formed from hexenuronic acid upon acid hydrolysis.

3. Determine if the hexenuronic acid content of kraft pulps can be influenced by AQ or polysulfide pulping technologies.

   Accomplishment : Preliminary studies, with a series of high-kappa hardwood pulps, suggested a potential dependency on AQ for hexenuronic acids but further studies need to be pursued to confirm this observation.

Biobleaching Studies - *A.J. Ragauskas*

The long term goal of this sub-project is to develop new methods of improving kraft bleaching operations employing enzymatic technologies.

Current Results: Research efforts over this past fiscal year have accomplished the three research goals established in the spring 1995 PAC, including:

1. Determine the fate of N-hydroxybenzotriazole after laccase-mediator (LM-stage) bleaching protocol.

   Accomplishment : PAC studies determined that greater than 99% of the mediator material could be recovered after a LM-stage. Additional studies determined that the bulk of the recovered material was 1-benzotriazole.

2. Study the biobleaching efficiency of an electron-rich and electron-poor benzotriazole derivative with laccase.

   Accomplishment: Several electron donating and withdrawing derivatives of benzotriazole were examined with laccase, to date, none have been found to be as effective as 1-hydroxybenzotriazole.

3. Examine the biobleachability of kraft pulps with varying levels of methoxy content employing the laccase-mediator bleaching system.

   Accomplishment: A softwood kraft pulp was methylated with several charges of dimethylsulfate. The methylated pulps were then reacted with the LM-stage. Although the efficiency of delignification appears to be influenced by the methylation procedure, further studies are needed to confirm this.

FUNDAMENTALS OF BLEACHING CHEMISTRY

High Efficiency Peroxide Bleaching

High Efficiency Peroxide Bleaching *by Art J. Ragauskas*

Executive Summary

Peroxide studies for the past fiscal year have focused on determining the relationship between peroxide delignification chemistry and the type of lignin present in the pulp. To accomplish this goal, we have examined the structure of residual lignin before and after peroxide bleaching of conventional and oxygen delignified softwood kraft pulps.

The results from peroxide bleaching of conventional and O_2 delignified kraft pulp suggest that a portion of lignin can be readily oxidized with alkaline peroxide. Lignin analysis indicates that the non-condensed phenoxy portion of lignin is most readily oxidized by peroxide and that the bleached residual lignin is enriched in condensed lignin structures. The structure of residual lignin after a D(EOP) was also examined this fiscal year. These studies noted substantial differences in lignin structure.

The delignification properties of an acidic pressurized peroxide stage were examined with a conventional southern softwood kraft pulp. Preliminary studies suggested that 50% delignification could be achieved by this procedure. Unfortunately, an acidic P*-stage was accompanied by a severe loss of viscosity, and further investigations were halted.

Research studies were also directed toward evaluating the intrinsic reactivity of lignin functional groups toward alkaline peroxide. As an initial study, a softwood kraft pulp was chemically enriched with ortho-quinones and then bleached with peroxide. Pulp bleaching studies suggested that a small improvement in delignification could be achieved if pulps were enriched with this functional group.

As an exploratory study, we briefly examined the effects of the counter-cation in alkaline peroxide bleaching and found that the extent of delignification varied according to the size of the cation. For a routine P-stage employing a 2% charge of hydrogen peroxide, the order of bleaching efficiency was $(CH_3)_4NOH$ > CsOH > KOH > LiOH > NaOH. Interestingly, this dependency on the counter-cation was diminished during a P*-stage.

Introduction

The bleaching chemistry of hydrogen peroxide has been an active component of PAC project F015 for the past five years. Prior studies in this field had focused principally on the activation of hydrogen peroxide delignification chemistry. The results of these investigations were summarized in a recent IPST Membership Report.

Over the past two years, our research interest has become increasingly focused on establishing the basic bleaching chemistry of hydrogen peroxide and process variations of this bleaching agent such as P* (Pressurized peroxide). The 1996 Spring PAC Review identified the fundamental bleaching chemistry of hydrogen peroxide as a research area of high interest. This report summarizes these activities.

Research Goals

The FY 1996-97 goals for this section of Project F015 are listed below:

1. Determine structure of residual lignin and bleach effluents after pressurized peroxide employing 2, 3, and 4% H_2O_2 on softwood kraft pulp.

2. Determine structure of residual lignin and bleach effluents after pressurized peroxide employing 1, 2, and 3% H_2O_2 on an oxygen delignified softwood kraft pulp.

3. Examine nature of residual lignin after Do(EOP).

4. Determine pH profile for P* at pH less than 7.0

5. Examine peroxide reactivity with quinone-enriched pulp.

Results

Goal 1: Peroxide Bleaching Softwood Kraft Pulp.

The bleaching chemistry of hydrogen peroxide was initially explored with a conventional softwood kraft pulp. Prior to bleaching, the pulp was chelated with EDTA. Table 1 summarizes the results of the Q-stage.

Table 1: Metals content[1] of softwood kraft pulp kappa number 28.4 before and after EDTA chelation.

Pulp	Cr	Mn	Fe	Ni	Al	Na	Mg	Ca
Before Q	<0.2	1.3	2.8	<0.3	4.1	1032	29.0	171
After Q	<0.2	0.4	3.1	<0.3	1.8	80	8.1	52.6

[1]mg of metal/kg od pulp.

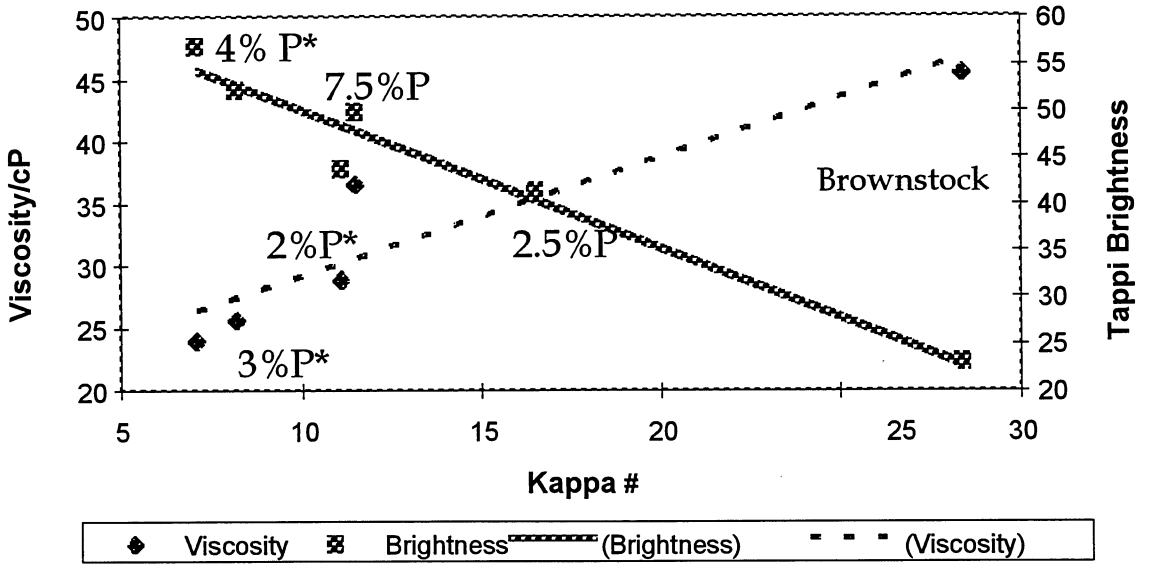
The chelated pulp was bleached with 2.0, 3.0, and 4.0% hydrogen peroxide at 110°C for 1 h. As a comparison, the pulp was also bleached with 2.5% H_2O_2 at 60°C for 4 h and 7.5% H_2O_2 at 70°C. The results of these studies are summarized in Table 2.

Table 2: Alkaline peroxide bleaching chelated, conventional softwood kraft pulp.

Bleaching Conditions	Kappa #	Acid content of pulp (meq./g odp)
Brownstock	28.4	0.088
2.0% P/110°C, 1h	11.1	0.085
3.0% P/110°C, 1h	8.2	0.079
4.0% P/110°C, 1h	7.1	0.078
2.5%P/60°C, 4h	16.5	0.100
7.5%P/70°C, 4h	7.1	0.096

The results of these initial investigations suggest that a 4.0% charge of peroxide at 110°C is equivalent to a 7.5% charge of peroxide at 70°C with respect to delignification. Interestingly, analysis of the acid content of the pressurized peroxide bleached pulps suggested that the less delignification occurring in a peroxide stage the more acid groups remain in the fiber. Presumably, this occurs due to a loss of acid groups into solution during a P*-stage. Because acid groups can favorably influence papermaking properties, the loss of acid groups in a P* stage may be significant and requires further investigation. Figure 1 summarizes the kappa number versus brightness and viscosity relationship found for the bleached pulps.

Figure 1: Changes in kappa number, brightness, and viscosity for peroxide bleaching softwood kraft pulp.



The bleaching chemistry of a peroxide stage was further examined by isolating residual lignin from the bleached pulps and characterizing lignin functional groups by advanced NMR methods. Residual lignin was isolated from the pulps by means of an aqueous acidic-dioxane solution, and typical yields were in the

range of 40-50%. The lignin samples were then purified and analyzed by ^1H NMR. The use of advanced NMR methods provides a quick and facile means of determining a variety of functional groups present in lignin, including acid groups, non-condensed phenoxy groups, condensed phenols, methoxy and aliphatic groups. Figure 2 provides a pictorial representation of lignin functional groups. Figure 3 presents a typical ^1H NMR of residual lignin.

Figure 2: Residual functional groups in kraft lignin.

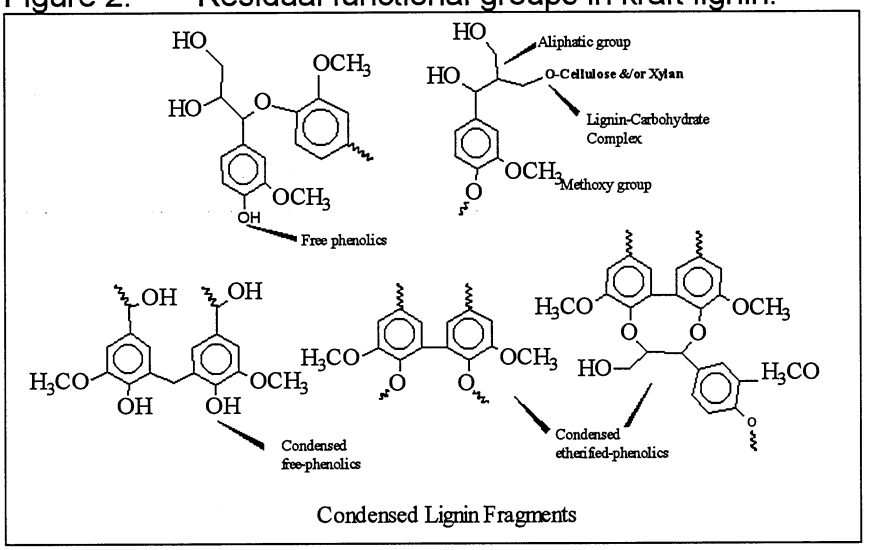
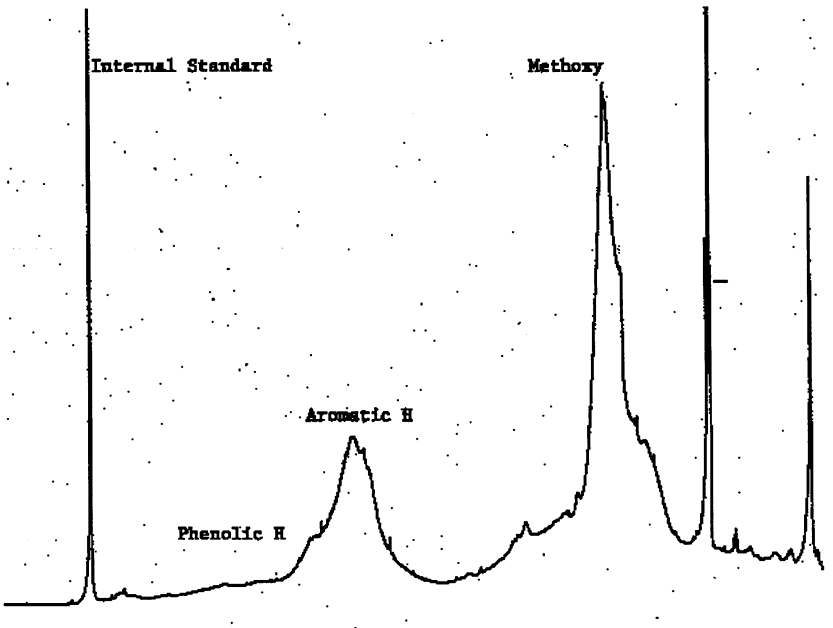


Figure 3: Typical ^1H NMR of residual lignin isolated from O2 delignified softwood kraft pulp via the acid dioxane extraction procedure.



The functional groups of lignin detected by NMR significantly influence the bleaching chemistry of hydrogen peroxide. For example, non-condensed phenoxy groups, in general, are very reactive with alkaline peroxide, whereas condensed phenoxy groups are believed to be not as reactive with hydrogen peroxide. The content of acid groups in lignin provides an indication of the oxidative severity of a given peroxide stage. Finally, increases in methoxy and aliphatic content are indicators of a lignin more recalcitrant to oxidation.

Figures 4 to 8 summarize the changes in lignin functional groups for the pulps described in Table 2. As expected, the acid group content of residual lignin increases as the charge of peroxide increases (see Fig. 4). Of greater significance is the observation that the amounts of acid groups contained in the lignin isolated from the pulp bleached with a 7.5% charge of peroxide at 70°C and with 2% peroxide under P* conditions differ dispite the comparable kappa numbers for these pulps. These differences could be due to different oxidative mechanisms in the overall bleaching chemistry of conventional peroxide and P*.

An inspection of the content of formyl groups in the residual lignin samples (see Fig. 4) indicates that the bleached pulps have a lower content of formyl groups than the unbleached pulp. The amount of formyl units varied little between bleached pulps. Currently, it is difficult to ascertain if this difference in formyl groups has any significance in peroxide bleaching chemistry.

Figures 5 and 6 indicate that the total phenoxy content is decreased during peroxide bleaching, and it appears that the loss in phenoxy content occurs more from the guaiacyl units than the condensed phenolic units. This result suggests that the condensed phenoxy groups are resistant to conventional and pressurized peroxide treatments. Analysis of the aromatic hydrogen content of residual lignin indicates (see Fig. 7) that this parameter initially decreases and then does not substantially change, suggesting that the condensed portion of lignin is relatively inert to peroxide. The methoxy content of residual lignin (see Fig. 6) increases initially and then remains essentially constant, indicating that residual lignin is enriched in methoxylated lignin. In summary, the results of this analysis indicated that the lignin remaining after a peroxide (conventional or pressurized) is becoming increasingly unreactive to hydrogen peroxide.

In summary, the results observed in this section suggest that low charges of peroxide remove most of the reactive lignin units available for an alkaline peroxide stage. The remaining lignin becomes increasingly less reactive. If the structural differences in lignin between conventional peroxide and P* bleached pulp are general, then this suggests that a P* can more effectively oxidize lignin, suggesting the benefits of pressurized peroxide are, in part, due to bleaching chemistry.

Figure 4: Formyl and acid content of residual lignins isolated from brownstock and peroxide bleached pulps.

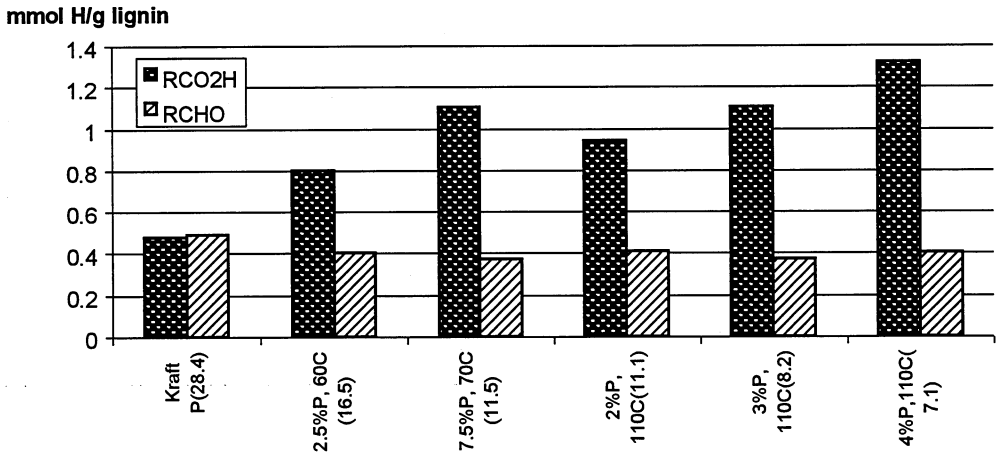


Figure 5: Changes in total phenoxy content and guaiacyl content of residual lignins isolated from peroxide bleached pulps.

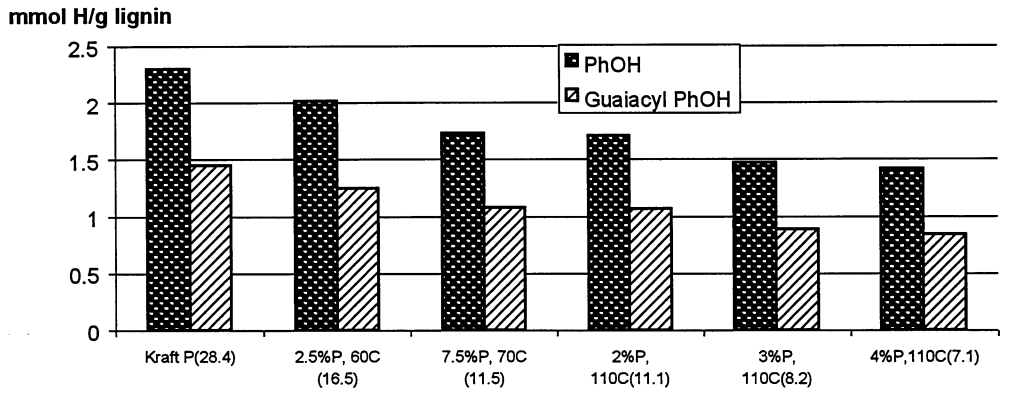


Figure 6: Changes in total phenoxy content and condensed phenolic content of residual lignins isolated from peroxide bleached pulps.

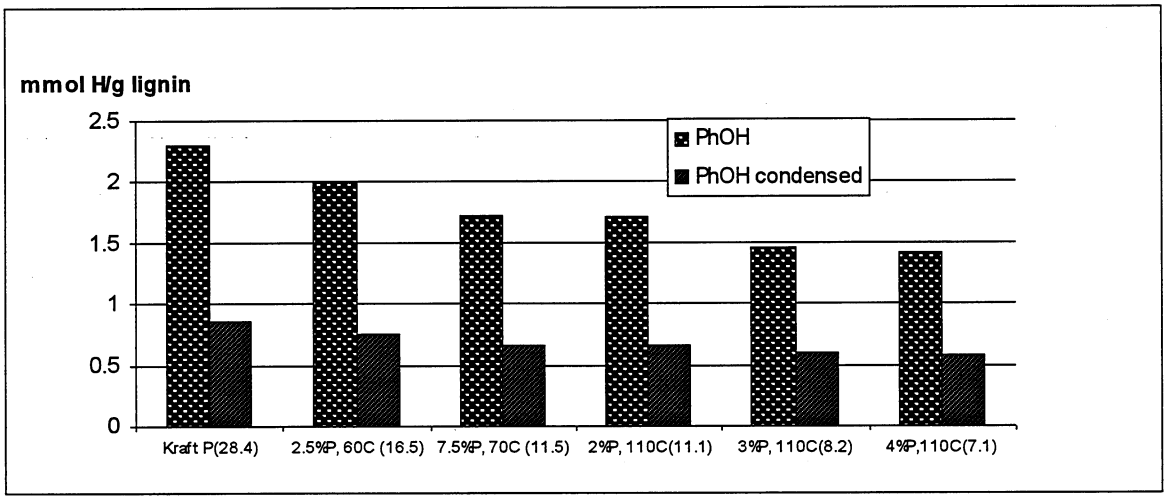
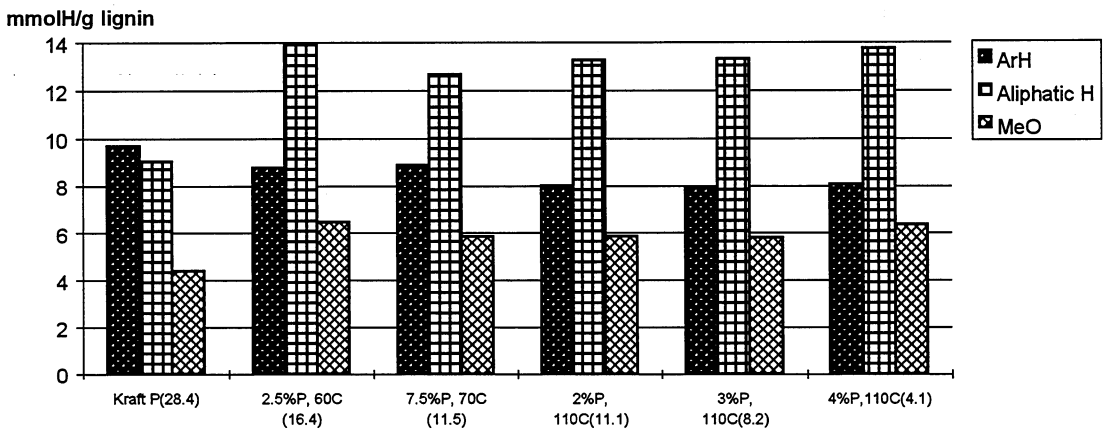


Figure 7: Changes in methoxy, aliphatic, and aromatic content of residual lignins isolated from peroxide bleached pulps.



Goal 2: Peroxide Bleaching O_2 Delignified Softwood Kraft Pulp.

As a follow-up to the brownstock peroxide bleaching experiments, we examined the peroxide bleaching chemistry of an oxygen-delignified kraft pulp. Following the experimental protocol described in the previous section, an O_2 delignified kraft pulp was chelated with EDTA (see Table 3) and then bleached under P* conditions employing 1, 2, and 3% charges of H_2O_2.

Table 3: Metals content[1] of oxygen delignified softwood kraft pulp kappa number 17.1 before and after EDTA chelation.

Pulp	Cr	Mn	Fe	Ni	Al	Na	Mg	Ca
Before Q	0.25	60.5	12.5	<0.4	18.3	865	454	1700
After Q	<0.18	0.35	3.77	<0.4	10.7	364	320	747

[1]mg of metal/kg od pulp.

Table 4: Physical properties of P* bleached oxygen delignified softwood kraft pulp. (110°C, 1 h, 50 psig).

Pulp	Kappa #	TAPPI Bright.	Viscosity/ cP	pH_{out}	Acid Content of Pulp (meq./gr od)	Yield %
starting	17.1	29.7	23.1	--	0.010	--
1% H_2O_2	10.0	54.8	18.6	9.5	0.069	99
2% H_2O_2	7.4	64.6	16.4	9.8	0.076	96
3% H_2O_2	6.3	79.2	12.7	10.0	0.082	96

As summarized in Table 4, a low charge of peroxide was effective at removing substantial amounts of lignin from the O_2 softwood kraft pulp. Interestingly, the acid content of the O_2 pulp was low, and the P*-stage was effective at increasing the acid content of the bleached pulp as summarized in Figure 8.

The changes in residual lignin structure after a P* stage were determined by isolating the residual lignin form the starting pulp and the P* bleached pulps. The residual lignin was extracted from the pulp by refluxing in an acidic aqueous dioxane solution for 2 h. On average, this process yielded approximately 55% of the lignin remaining in the pulp. After purification, the lignin samples were analyzed by ^1H NMR for formyl, phenolic, acid, aromatic hydrogen, alipthatic and methoxy groups. These analyses are summarized in Figures 9 thru 11.

Figure 8: Acid content of kraft after O_2 and P* bleaching.

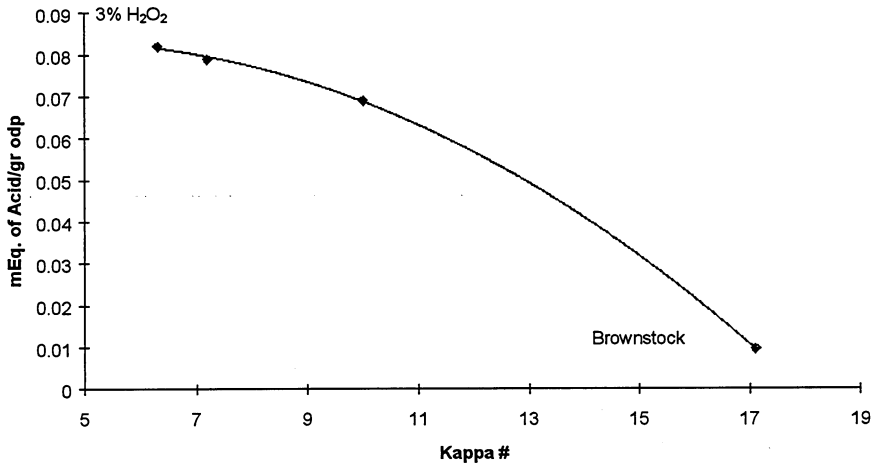
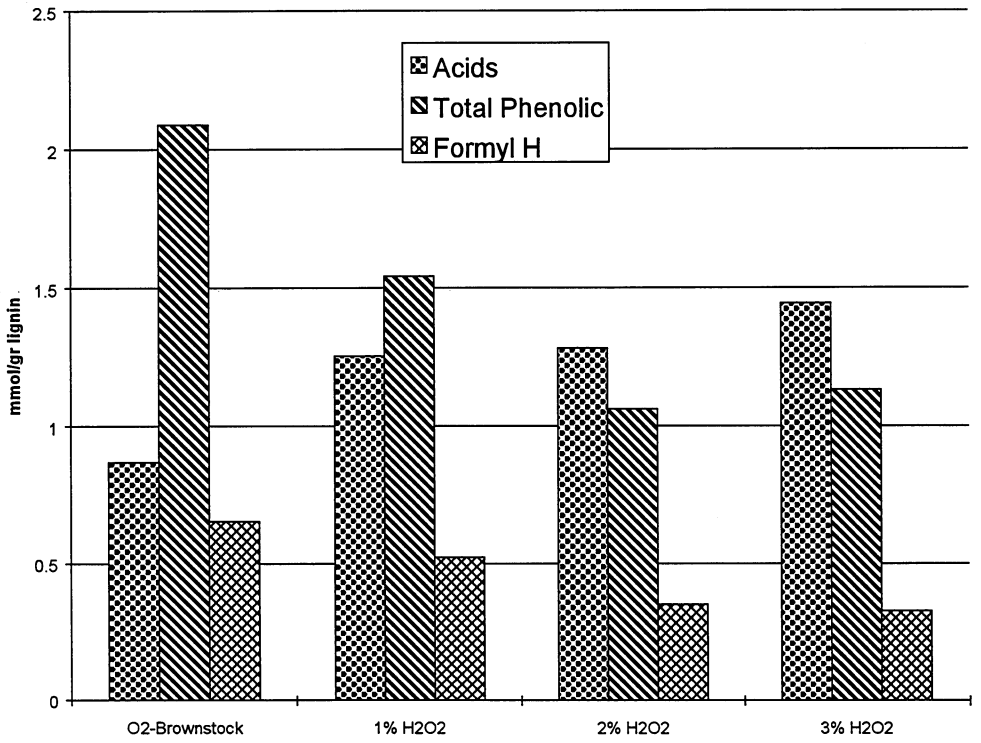
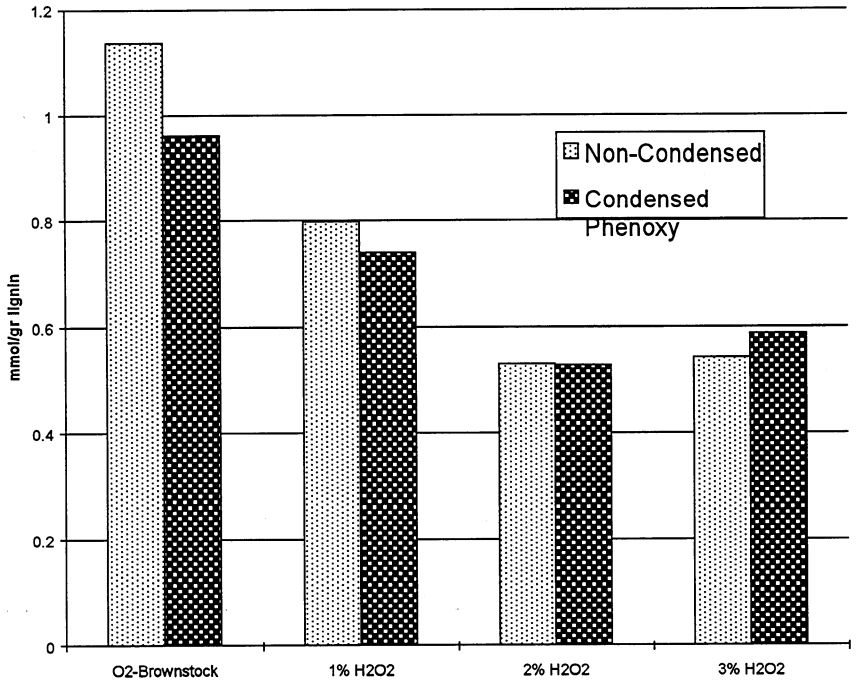


Figure 9: Acid, formyl, and phenoxy group content of P*-bleached O_2 softwood kraft pulp.[1]



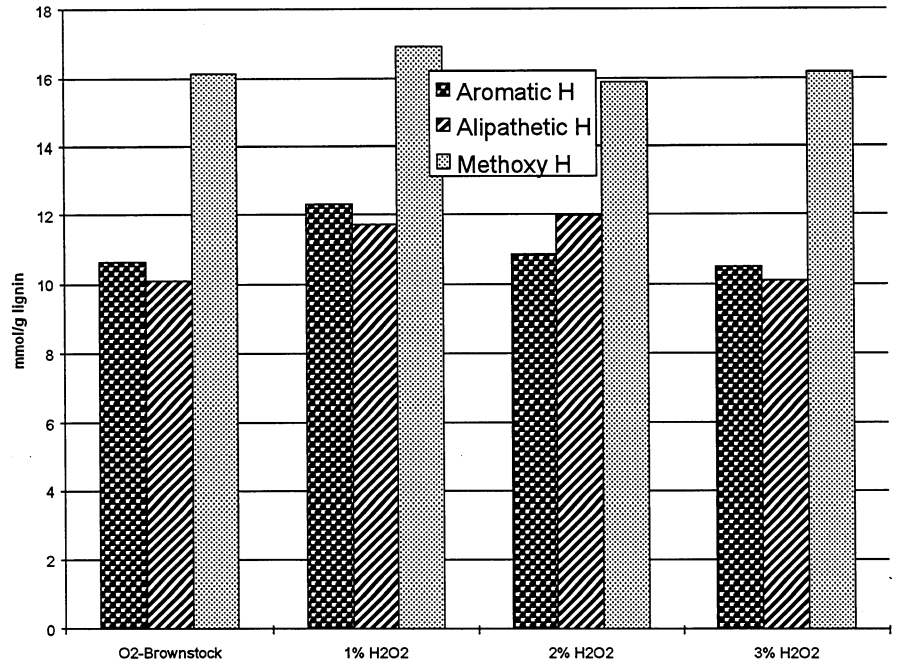
[1]see Table 4 for further descriptions of the pulps.

Figure 10: Total and Condensed phenoxy group content of P*-bleached O_2 softwood kraft pulp.[1]



[1]see Table 4 for further description of the pulps.

Figure 11: Acid, formyl, and phenoxy group content of P*-bleached O_2 softwood kraft pulp.[1]



[1]see Table 4 for further description of the pulps.

Analysis of the data in Figure 9 indicates that the acid content of the residual lignin is increased as the charge of peroxide is increased for the P*-stage. A comparison of the acid content of the starting O_2-delignified kraft pulp (see Fig. 9) and the acid group content of the softwood kraft pulp (see Fig. 4) [Note these are two different commercial pulps] indicated that the lignin from the oxygen delignified pulp was higher in acid group content. Although this result was to be expected, it validates the analytical techniques employed in this study.

An examination of the phenoxy content of P* bleached O_2 pulps suggested that the phenolic content decreased after a P*-stage (see Fig. 9). Figure 10 dissects the phenoxy content into condensed and non-condensed phenoxy units. It becomes clear from this analysis that the non-condensed are much more reactive under a P*-stage than condensed phenoxy groups.

The results of quantifying the aromatic, methoxy and aliphatic groups suggest that the amounts of these groups in bleached residual lignin increases slightly with a low charge of peroxide and then gradually decrease. Because hydrogen peroxide cannot readily degrade these types of lignin functional groups, it was expected that these structures would not change substantially during a P*-stage.

The results of these studies suggest that the O_2-stage has, to some extent, reduced the reactivity of the residual lignin toward a P*-stage. Hence, the pulp has a lignin with less non-condensed phenoxy units and this detrimentally impacts on peroxide bleaching. Given the relative reactivity of lignin with hydrogen peroxide, our results suggest that a potentially more effective method of utilize hydrogen peroxide would be to allow for a conventional peroxide stage to occur initially, followed by a pressured stage. In this manner, the most reactive lignin units would be consumed "up-front," and the use of the high temperature conditions could then be employed to remove less reactive lignin units. (Note: in essence this would be an inverted P_{HT} process).

NOTE: The effluents from peroxide bleaching, the oxygen delignified and conventional softwood kraft were collected, purified and analyzed by ^1H NMR. The analysis of this data is ongoing as several unassignable signals are apparent in the spectra and additional studies are required.

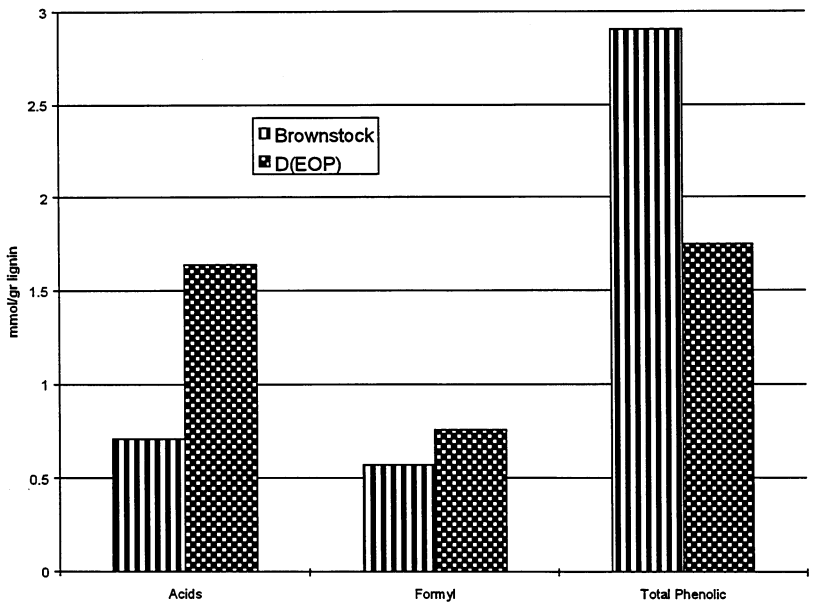
Goal 3: Residual Lignin from D(EOP) Bleached Softwood Kraft Pulp.
Changes in residual lignin structure before and after a D(EOP) treatment for a conventional softwood kraft pulp were determined employing a commercial southern softwood, kappa number of 31.4. The pulp was bleached with a 0.21 kappa factor following standard ClO_2 bleaching conditions. After bleaching, the pulp was washed and alkaline extracted under typical (EOP) conditions. The results of these bleaching reactions are summarized in Table 5.

Table 5: Bleaching parameters for D(EOP) treatment of a southern softwood kraft pulp.

Pulp	Conditions	Kappa #	TAPPI Brightness	Viscosity/ cP
Starting		31.4	26.0	34.6
After D0	0.21 kf, 50°C, 50 min., 2.0 pH_{out}, 10% csc			
After (EOP)	3.2% NaOH, 75 min., 75°C, 0.5%P, 10%csc	3.7	62.3	22.4

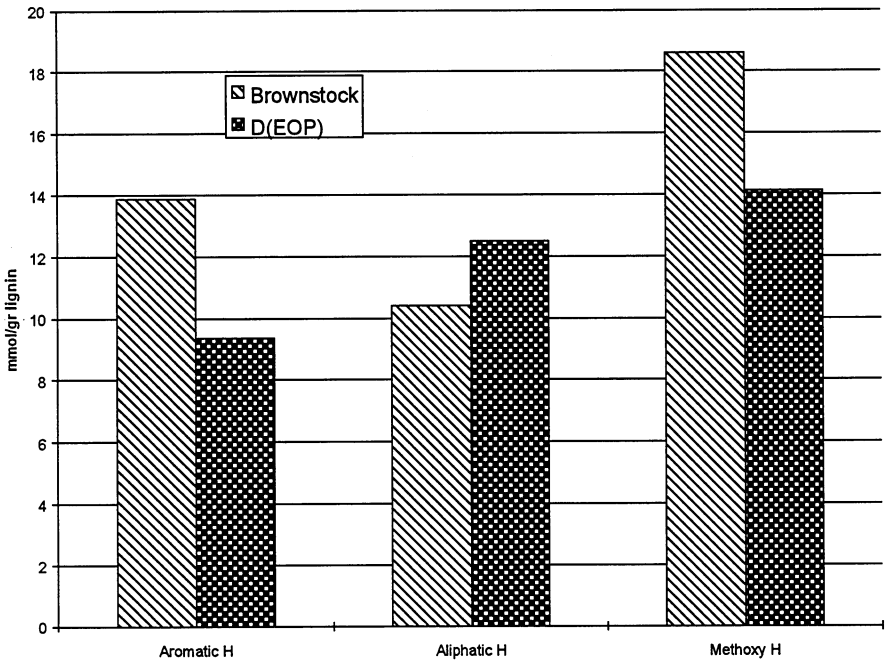
After D(EOP), the residual lignin in the pulp was isolated employing an acidic dioxane extraction stage. The isolated lignin was analyzed by ^{1}H NMR, and these results are summarized in Figures 12 and 13. In comparison to the P* stages examined previously, the D(EOP) treatment virtually doubled the amount of acid groups remaining in the lignin and the phenoxy content of the bleached residual lignin was decreased by 40%. The content of aromatic hydrogen and methoxy groups (see Fig. 13) was significantly decreased presumably due to the presence of small amounts of chlorine present during the Do stage. Further, more detailed studies will be required to ascertain what specific lignin functional group changes occur due to the Do and (EOP) stages. Studies directed at addressing this issue will be proposed for the next fiscal year.

Figure 12: Changes in acid, formyl, and phenoxy content of conventional kraft after bleaching with D(EOP).[1]



[1]see Table 5 for further description of the pulps.

Figure 13: Changes in aromatic, aliphatic, and methoxy proton content of a conventional softwood kraft after bleaching with D(EOP).[1]



[1]see Table 5 for further description of the pulps.

Goal 4: Acidic Pressurized Peroxide.

The delignification potential of a pressurized acidic peroxide stage was examined employing a softwood kraft pulp. Prior to the bleaching studies, the pulp was EDTA chelated, and the results of the Q-stage are summarized in Table 6.

Table 6: Metal profile[1] of kraft pulp before and after standard EDTA chelation stage.

Pulp	Cr	Mn	Fe	Ni	Al	Na	Mg	Ca
Pre-Q	1.20	45.0	44.2	0.70	6.10	47.4	157	1554
Post-Q	0.60	0.90	38.7	<.3	5.60	161	113	634

[1]mg of metal/kg od pulp.

The chelated pulp was bleached under pressurized peroxide conditions employing a 2.0% charge of H_2O_2 at 110°C for 1 h. The starting pH was varied from 10.7 to 3.5. After bleaching the pulps were characterized according to kappa number, viscosity, TAPPI brightness, and yield (see Table 2). The pulps bleached at pH values less than 7 were then extracted with alkali and physical properties were re-evaluated. The results of these investigations are summarized in Tables 7 and 8.

Table 7: Peroxide bleaching softwood kraft pulp[1] employing 2.0% H_2O_2 at 110°C for 1h.

Bleaching conditions, starting pH	Kappa #	TAPPI Brightness	Viscosity/cP	pH_{out}	Yield
10.7	10.7	47.1	13.1	9.7	96.4
5.0	18.1	28.0	2.9	2.9	95.5
4.5	16.9	27.2	3.1	2.6	93.4
4.0	17.8	26.8	2.6	2.5	92.9
3.5	16.3	26.6	2.9	2.6	94.9

[1]starting kappa #: 24.0, viscosity: 27.1 cP, TAPPI brightness: 28.8.

Table 8: Alkaline extraction[1] of peroxide bleached softwood kraft pulp[1] employing 2.0% H_2O_2 at 110°C for 1h.

$pH_{initial}$ of peroxide stage	Kappa #	TAPPI Brightness	Viscosity/cP
5.0	12.3	36.6	2.8
4.5	12.2	35.4	2.9
4.0	11.4	35.4	2.5
3.5	13.2	34.8	2.8

[1]2% NaOH, 70°C, 10% consistency.

Analysis of the pulps after the P-stage indicated that the acidic P* bleached pulps had undergone a substantial loss in viscosity. Given these results, no further work was pursued in this field of research.

Goal 5: Lignin Activation.

Recent studies in the PI's laboratory on the nature of residual lignin suggest that a portion of lignin present in kraft pulps is readily oxidizable by hydrogen peroxide (ca 30-50%); the remaining lignin needs much more forcing conditions for its removal. As a preliminary investigation into new methods of enhancing the delignification properties of hydrogen peroxide, it was proposed at the last PAC that specific functional groups could be introduced into lignin to enhance its reactivity with hydrogen peroxide. Changes in peroxide delignification could then be correlated to specific functional groups in lignin.

As an initial investigation into this aspect of peroxide bleaching chemistry, we elected to employ a softwood kraft pulp chemically enriched with ortho-quinones. A chelated, softwood kraft pulp (see Table 9 for metals profile) was treated with Fremy salt, a reagent known to convert free phenoxy groups into the corresponding ortho-quinine structure (see Fig. 14).

Figure 14: Fremy salt oxidation of lignin-like structures.

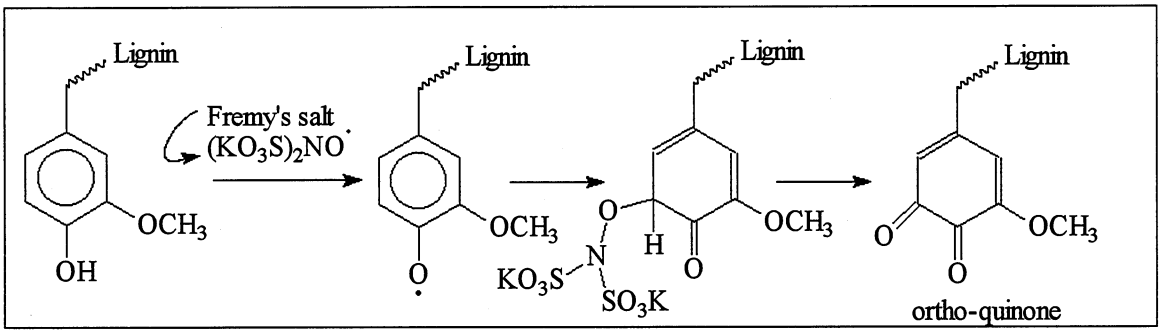


Table 9: Metal profile of kraft pulp[1] before and after metal chelation with EDTA.

Pulp	Cr	Mn	Fe	Ni	Al	Na	Mg	Ca
Pre-Q	0.28	33.9	67.1	<.5	6.15	182	225	2080
Post-Q	0.24	1.54	41.0	<.5	4.61	62.7	166	1000

[1]mg of metal/kg od pulp.

Analysis of the klason lignin content pre- and post-Fremy salt treatment suggested that the Fremy oxidation did not remove any lignin (see Table 10). The kappa number of the pulp did change as to be expected if ortho-quinone groups were introduced into lignin.

Table 10: Klason content and kappa number of softwood kraft before and after Fremy salt treatment.

Pulp	Klason Lignin	Kappa #
Pre-Fremy salt treatment	4.0%	33.5
Post-Fremy salt treatment	4.0%	28.4

The pre- and post-Fremy salt treated kraft pulps were then bag bleached with a 1%, 2% , and 3% charge of hydrogen peroxide under alkaline conditions at 70°C for 4 h. The results of these studies are summarized in Table 11.

Table 11: Peroxide delignification of pre- and post-Fremy salt treated softwood kraft pulp.

Bleaching Conditions	Starting Kappa #	Bleached Kappa #	TAPPI Brightness	pH_{out}	Carboxy Content of Pulp
1% P	33.5	25.2	37.9	9.8	0.098
1% P	28.4 Fremy pulp	23.8	37.6	9.5	0.102
2% P	33.5	21.0	46.1	10.6	0.098
2% P	28.4 Fremy pulp	20.2	41.2	10.8	0.100
3% P	33.5	18.2	50.5	11.4	0.098
3% P	28.4 Fremy pulp	17.8	44.3	11.5	0.098

The results of the bleaching studies suggest that enrichment of kraft pulps with quinoid-lignin units provides a modest increase in the delignification properties of hydrogen peroxide. Future proposed studies will examine alternative methods of lignin activation.

Effect of Counter Cation on Alkaline P Delignification.

The effects of the counter-cation in alkaline peroxide bleaching were preliminary investigated by treating a softwood kraft pulp with a 2% charge of hydrogen peroxide and a 1.6% charge of NaOH or its molar equivalence of LiOH, KOH, CsOH, or $(Me_4N)OH$ at 70°C for 4 h and for 1 h at 110°C. (see Table 12)

Table 12: Effect of counter cation on an alkaline peroxide stage employing 2.0% charge of H_2O_2 .

Bleaching Conditions	% Delignification - employing 1.6% Charge NaOH or molar equivalent of MOH				
	NaOH	LiOH	KOH	Me_4NOH	CsOH
70°C, 4 h	36	37	39	41	43
110°C, 1 h	56	--	57	--	59

On average, the effects of the counter cation on a routine P-stage were minor, although it is interesting to note, that the larger and more diffuse the cation becomes, the more effective the alkali peroxide stage. The small differences observed for a P-stage were further diminished under pressurized peroxide conditions.

Although the observed effects of varying the counter cation were minor, it is anticipated that the metals profile during mill closure could substantially influence peroxide bleaching chemistry. The changes observed in this study would not be relevant to closed mill studies because this study examined only

Group 1 and 2 metals and not the more harmful transition-based metals such as Fe and Mn. Future proposed studies will examine these issues.

Experimental:

Materials: Commercial softwood kraft pulps were acquired from several pulping mills in the US. All chemicals were purchased from commercial vendors and used as received.

Methods

Bleaching Studies: Conventional peroxide bleaching studies were performed in sealed plastic bags. All alkaline peroxide studies employed $MgSO_4$ as a viscosity protection agent, the mass ratio of H_2O_2 to $MgSO_4$ was 50:1. The P* bleaching reactions were performed in a peg mixture. The pressure was held constant at 50 psig with N_2. All bleaching reactions were accomplished at 10% consistency.

Chlorine dioxide bleaching studies were performed at 10% consistency, following standard methods in a sealed plastic bag.

Lignin Isolation Procedure: Air-dried pulps were extracted with a 9:1 dioxane/aqueous acid solution (0.1 N HCl). The extraction was performed at 8% consistency and refluxed for 2 hrs under an argon atmosphere. The mixture was then filtered, and the filtrate was filtered. The solution was neutralized and concentrated under reduced pressure. After the volume was reduced to less than 10% of the original volume, 200 mL of distilled water was added three separate times and reconcentrated. The lignin solution was then acid precipitated by lowering the pH to 2.5 with HCl. The acid-precipitated lignin was then washed several times with distilled water and freeze-dried.

^{1}H NMR Analysis of Residual Lignin: The structural features of lignin were characterized by means of ^{1}H-NMR employing a Bruker 400-MHz DMX NMR spectrometer. Quantitative ^{1}H NMR analysis of lignin samples was accomplished at 50°C in d_6-$DMSO_3$. Acquisition parameters included: 90° pulse, 17 ppm sweep width, 25s delay and 800 acquisitions. TMS and pentafluoro-benzaldehyde were added to each NMR sample as a shift reference and as an internal standard for quantification, respectively.

Analytical Methods: Kappa number, TAPPI brightness and viscosity determ-inations were performed following TAPPI standard procedures. Metals analysis was determined by ICP emission spectroscopy.

Future Recommendations:

The results of the past year have established the value of determining the structure of residual lignin during peroxide bleaching. Although several research avenues are available, based on our results to date, research issues that should in the next fiscal year include:

- Examine effects of "inverted P_{HT} sequence" for delignification;
- Examine bleaching chemistry between P and D;
- Chemical modification of lignin to enhance peroxide delignification;
- Study bleaching chemistry of hydrogen peroxide applied on fully bleached pulp to minimize reversion.

The goal of these proposed studies would be to develop the fundamental knowledge needed to improve peroxide usage in ECF bleaching scenarios.

Research Benefits:

The anticipated benefits of these studies include:

- reduced bleaching costs;
- reduced AOX generation;
- improved pulp properties and mill operations.

Related Project Studies:

Project Title: High Efficiency ClO_2 Delignification
Funding Source: DOE, 2020 Program
Principal Investigators: Dr. A.J. Ragauskas & Dr. T.J. McDonough

Research Objectives: The overall objective of this proposal is to develop a fundamental understanding of the mechanisms of chlorine dioxide delignification of low-kappa kraft pulps and identify new methods of improving the efficiency and effectiveness of this bleaching agent. This goal will be accomplished in a three fold manner:

- Determine the nature of residual lignin/chlorine dioxide reactions that contribute to the success of improved ClO_2 bleaching protocols such as rapid D_o;
- Identify the residual lignin fragments resistant to ClO_2 and modify D_o stage to enhance lignin reactivity;
- Enhance ClO_2 delignification with chemical treatments prior to a D-stage.

These goals will be established by evaluating the fundamental structural changes that occur in lignocellulosic material upon reaction with chlorine dioxide. The results will then be employed to develop new bleaching technologies that will permit enhanced delignification while simultaneously reducing the generation of chlorinated organic compounds.

IPST Ph.D. Student Research:

Project Title: The Chemistry of Alkaline Extraction Stages between Chlorine Dioxide Stages

Student: Troy Runge

Until recently, an alkaline extraction stage was viewed as a simple extraction of lignin after a D or C-stage. The need to improve delignification and enhance final brightness properties of fully bleached pulps has lead to substantial changes in the first extraction stage with either oxygen and/or peroxide now being routinely added to this process. These process changes have considerably altered the types of chemistry occurring during E, (EO) or (EOP). This project will establish the fundamental bleaching chemistry occurring during these oxidatively reinforced alkaline extraction stages.

Project Objectives:

1. Investigate fundamental reactions occurring in the alkaline extraction stage with various oxidant reinforcements. Research efforts will focus primarily on changes in lignin structure and molecular weight properties.

2. Characterize physical pulp properties to evaluate benefits of the observed lignin structural changes.

3. Investigate several new NMR spectroscopic techniques designed to provide information on aromatic and aliphatic carbonyl structures.

Benefits of Project:

1. Increased fundamental understanding of the alkaline extraction stage will allow further optimization.

2. Direct comparison of the chemistry and pulp properties of various oxidative alkaline extraction stages (E vs. EO vs. EOP).

3. Fundamental principles discovered in this study will permit rational design of new and improved pulp bleaching operations.

FUNDAMENTALS OF BLEACHING CHEMISTRY

Influence of Hexenuronic Acids on Bleaching

Influence of Hexenuronic Acids on Bleaching *by Art J. Ragauskas*

Executive Summary

Research efforts over the past fiscal year examined a series of commercial hardwood and softwood kraft pulps for hexenuronic acids. These studies determined that for low-kappa hardwood kraft pulps hexenuronic acids contribute approximately 50% to the apparent kappa number of the pulp. For softwood kraft pulps, the results were more variable, but it appears that hexenuronic acids contribute approximately 15% of the total kappa number. Detection of hexenuronic acids can be indirectly monitored by employing an acid hydrolysis procedure and UV analyzing the effluents. Metals analysis of kraft pulps before and after an acid treatment stage indicates a substantial drop in metals content for the post-treated pulps. These results suggest that hexenuronic acids may be involved in the overall metal affinity mechanism for kraft pulps. Preliminary bleaching studies indicate that the presence of hexenuronic acids in pulp results in the consumption of bleaching chemical.

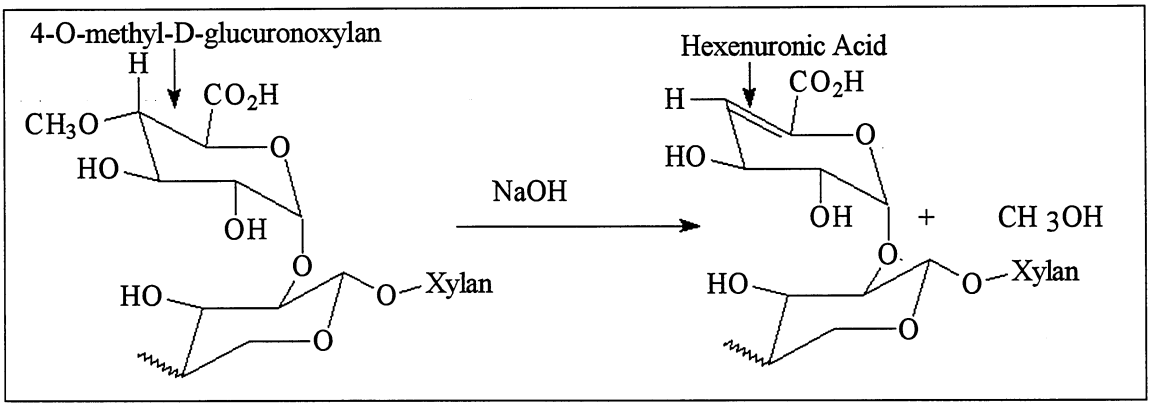
Introduction

The 1996 Spring PAC Review identified the pulping-bleaching chemistry of hexenuronic acids as a research area of high interest. This report will briefly review the past research efforts in this field and summarize recent studies in Ragauskas' laboratory.

Literature Overview

Base catalyzed formation of hexenuronic acids from 4-O-methyl-D-glucuronxylan (see Fig. 1) has been known in the literature for more than 20 years. Research by Clayton (Svensk Papperstidning, Feb., p 115,1963) suggested the formation of hexenuronic acids from hemicelluloses under alkali conditions. These early studies examined the behavior of 4-O-methyl-D-glucuronoxylans from poplar, white birch, and white elm with alkali at 170°C and found indirect evidence for the formation of hexenuronic acids.

Figure 1: Alkali-catalyzed formation of hexenuronic acids.



Subsequent studies by Johansson and Samuelson (Carbohydr. Res., 54, p 295, 1977) and Simkovic et al. (Carbohydr. Res., 152, p 137, 1986) found additional experimental evidence supporting the formation of hexenuronic acids from glucomethyl-D-glucuronic acid derivatives. Finally, Teleman et al. (Carbohydr. Res., 280, p 197, 1996 and Carbohydr. Res., 293, p 1, 1996) isolated and characterized the presence of hexenuronic acids in kraft pulps.

Studies by Vuorinen et al. (Conf. Proceedings from 1996 Int. Pulp Bleach. Conf., 1, p 43, 1996) and Buchert et al. (Tappi J., 78, p 125, 1995) further explored the chemistry of hexenuronic acids in kraft pulps. It was demonstrated that in birch kraft pulps hexenuronic acids contributed up to 50% of the kappa number of the pulp; consumed electrophilic bleaching chemicals such as chlorine dioxide and ozone; contributed to the binding of metals to pulp and were a principal factor involved in the formation of oxalic acid. Hence, hexenuronic acids play a pivotal role in bleaching, metals management, and mill closure. Based on these considerations, the 1996 Spring PAC elected to examine the chemistry of hexenuronic acids in Project F015.

Research Goals

The FY 1996-97 goals for this section of F015 are listed below:

1. Examine the contribution of hexenuronic acids toward the kappa number of softwood and hardwood kraft pulps.

2. Develop an experimental method to directly quantify hexenuronic acids in pulp.

3. Determine if the hexenuronic acid content of kraft pulps can be influenced by AQ or polysulfide pulping technologies.

These research goals have been accomplished over this past fiscal year, and the results of these investigations are summarized in this report.

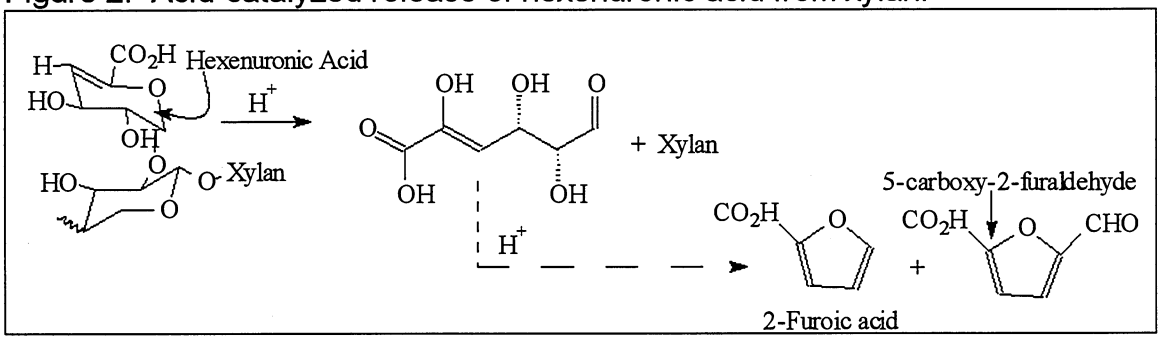
Results

Goal 1: Contribution of hexenuronic acids toward kraft pulp kappa number.

As an initial research goal in this project, it was recommended by PAC that a quick survey study be performed on a variety of commercial kraft pulps to determine the relevancy of hexenuronic acids to North American bleaching operations. Analysis of the hexenuronic acid content of kraft pulps was initially determined by employing an acid hydrolysis procedure. Prior studies by Teleman et al. (Carbohydr. Res., 280, p 197, 1996) had established that hexenuronic acids could be removed from pulp by an acid treatment. The proposed mechanism for this reaction is shown in Figure 2. (Note: An important

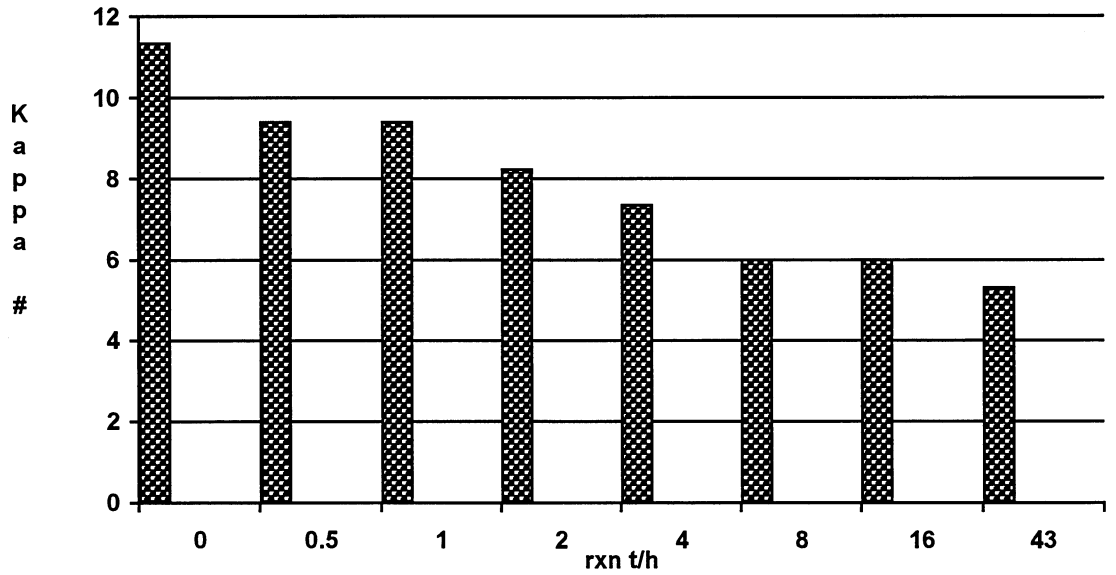
assumption of the acid hydrolysis method is that the procedure does not contribute to the removal of lignin.)

Figure 2: Acid-catalyzed release of hexenuronic acid from xylan.



Preliminary studies examined the acid hydrolysis behavior of a commercial hardwood kraft pulp refluxed in a pH 3.5 aqueous solution of formic acid/sodium formate for an extended time period. Figure 3 summarizes the results of these studies.

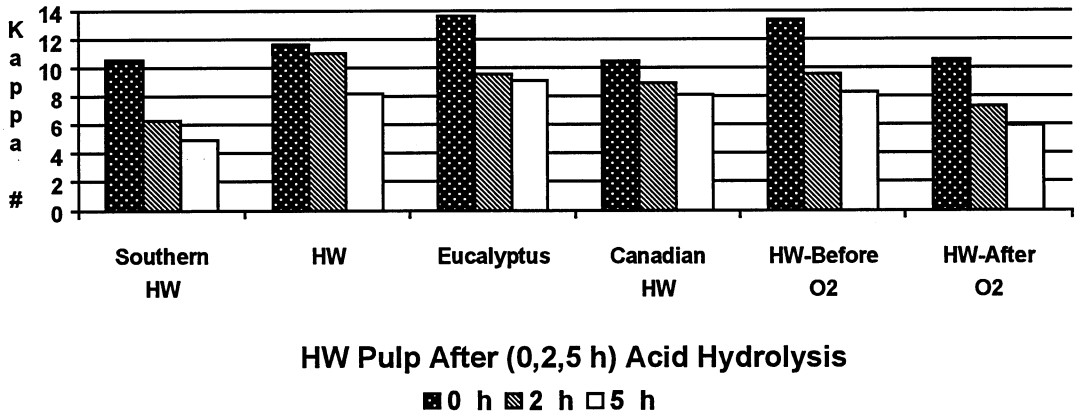
Figure 3: Kappa number of a commercial hardwood kraft pulp before and after refluxing in aq. formic acid-sodium formate solution.



The results of this initial study suggested that approximately 53% of the kappa number of this hardwood kraft pulp was due to hexenuronic acids and not residual lignin. Following this initial study, it was decided to measure the apparent kappa number of the kraft pulps after 2 and 5 h of reflux in a formic

acid solution. The results of these investigations are summarized in Figures 4 - 6.

Figure 4: Kappa number of commercial HW kraft pulps before and after refluxing in aq. formic acid-sodium formate solution for 2 and 5 h.



Analysis of the hardwood data suggests that hexenuronic acids contribute approximately 20 to 60% of the total kappa number for hardwood kraft pulps. Furthermore, the ease of acid-catalyzed removal of hexenuronic acids varies substantially for the pulps examined. For some of the hardwood kraft pulps examined, it appeared that the hexenuronic acids are substantially removed after two hours of acidic treatment, whereas other pulps required five hours. The factors contributing to this phenomenon are currently not understood. Acid hydrolysis of softwood kraft pulps (see Figures 5 & 6) suggested that the hexenuronic acids contributed approximately 0 to 15% of the total kappa number for these pulps.

Figure 5: Kappa number of commercial softwood kraft pulps before and after refluxing in aqueous formic acid-sodium formate solution for 2 and 5 h.

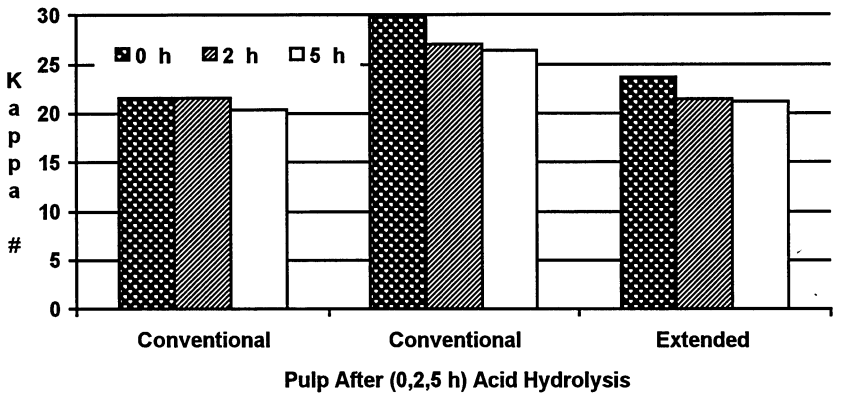
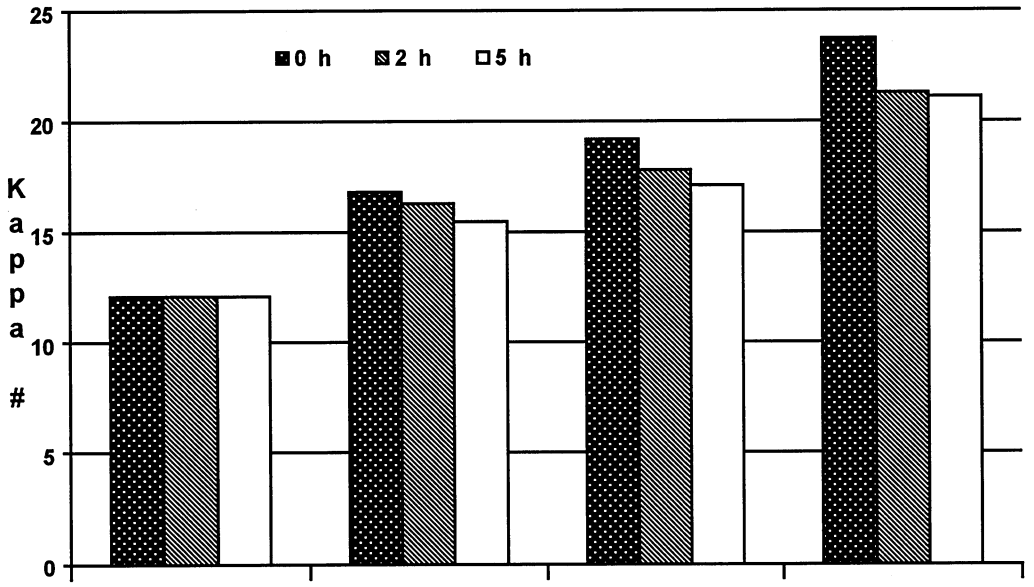
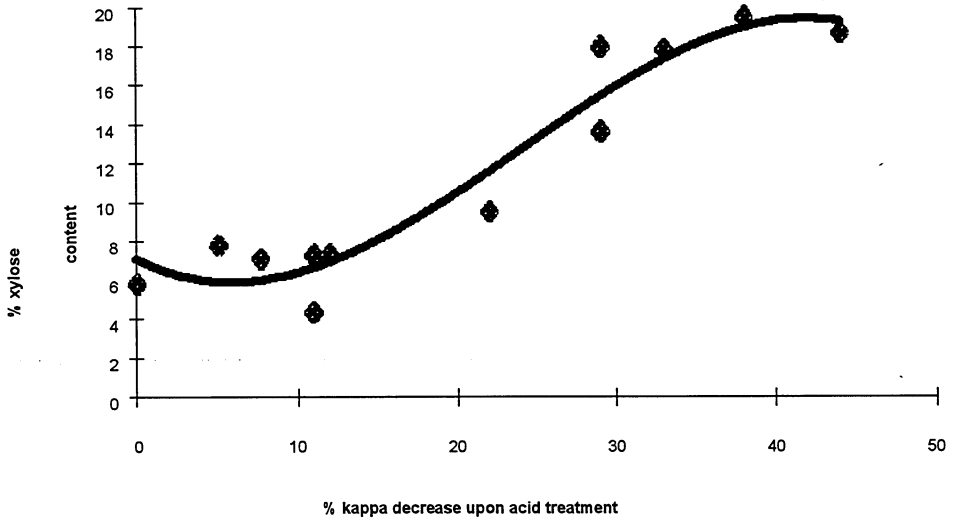


Figure 6: Kappa number of laboratory prepared, extended modified softwood kraft pulps before and after refluxing in aqueous formic acid-sodium formate solution for 2 and 5 h.



Along with the kappa number analysis of each starting pulp, the xylan content of each starting pulp was determined. Analysis of the xylan content versus the drop in kappa number, after acid hydrolysis, suggested a correlation between the xylan content of the starting pulp and the contribution of hexenuronic acids to the kappa number of the pulp (see Fig. 7).

Figure 7: Relationship between xylan content of softwood and hardwood kraft pulps and the decrease of kappa number upon acid hydrolysis treatment.



The acid hydrolysis conditions employed in these initial studies was detrimental to pulp viscosity as shown in Figures 8 and 9. These data do not preclude the use of an acid treatment to remove hexenuronic acids, and Vuorinen et al. (Conf. Proceedings from 1996 Int. Pulp Bleach. Conf., 1, p43, 1996) have developed a pressurized acid treatment that can be employed to remove these unsaturated sugars from pulp.

Figure 8: Relative changes in viscosity and kappa # of hardwood kraft pulps upon treatment with acid for removal of hexenuronic acid.

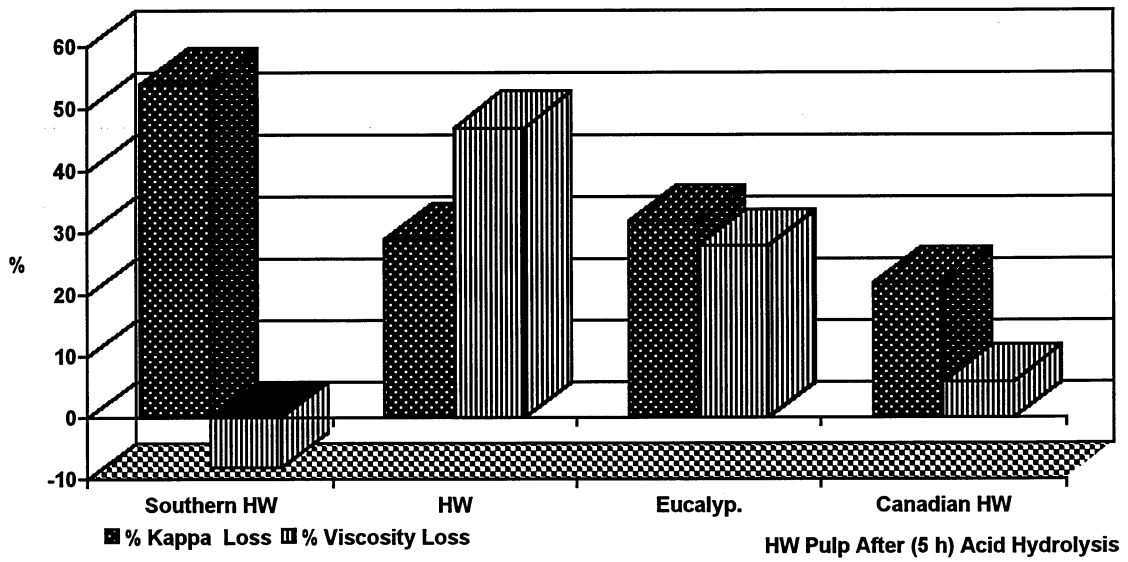
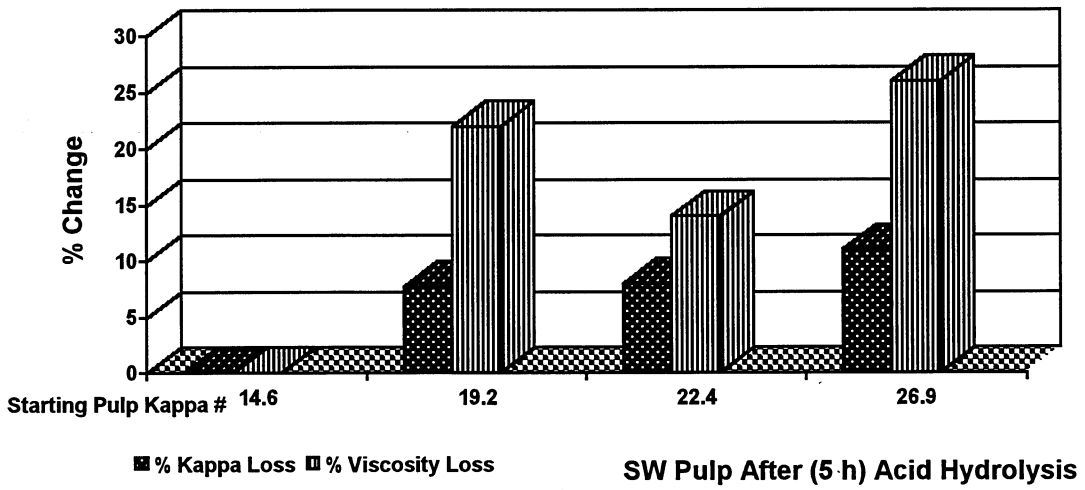


Figure 9: Relative changes in viscosity and kappa # of softwood kraft pulps upon treatment with acid for removal of hexenuronic acid.



The results of these analyses clearly demonstrated that hexenuronic acids are a substantial component of the kappa number for hardwood kraft pulps in North American pulp operations and a minor component of softwood kraft pulps.

The influence that hexenuronic acids have on bleaching was investigated by employing a softwood and hardwood kraft pulp with chlorine dioxide and ozone. As summarized in Figure 10, acid treatment of the oxygen delignified hardwood kraft pulp allowed for a 100% increase in the extent of delignification by ozone. Performing the same type of experiment for a softwood kraft pulp suggested that acid pretreatment of a kraft pulp could enhance ozone delignification by 50% (see Fig. 11).

Figure 10: Ozone bleaching post-O_2 hardwood kraft pulp and acid-washed post-O_2 hardwood kraft pulp.

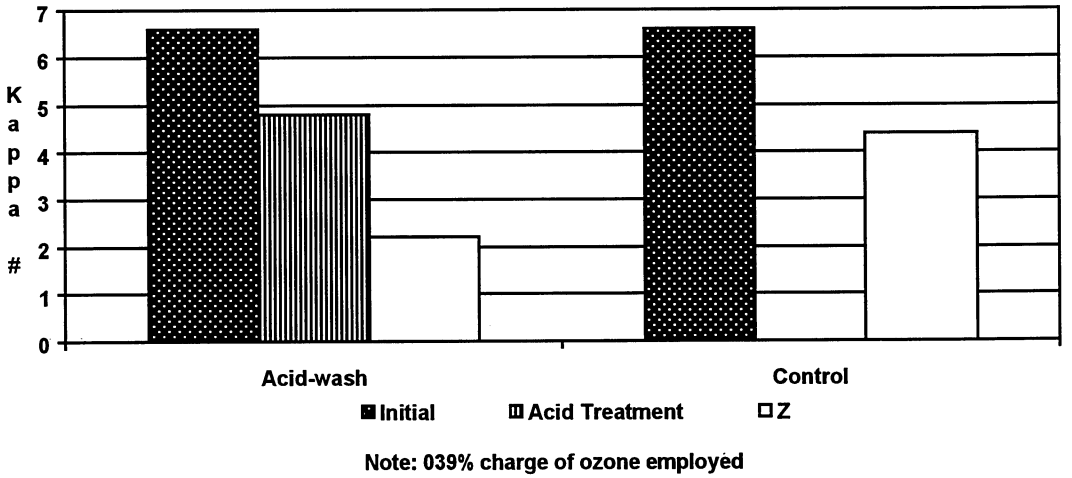
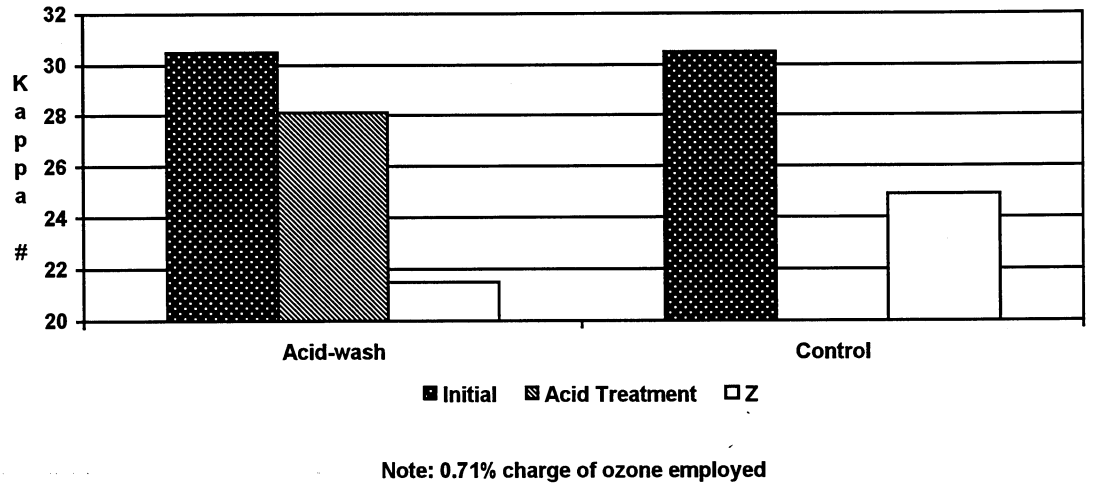
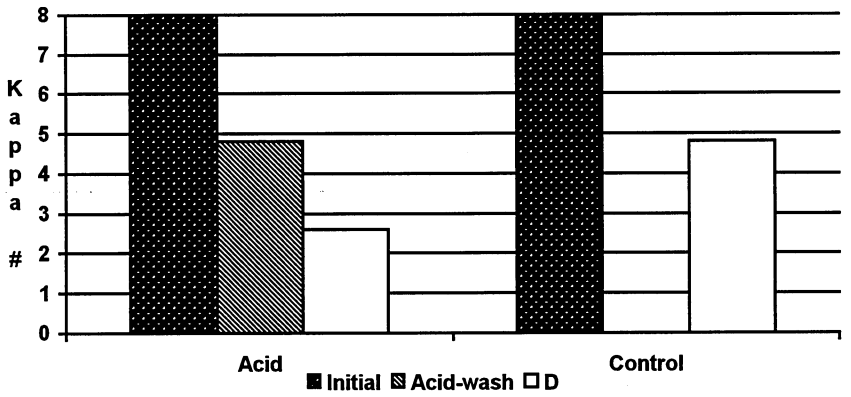


Figure 11: Ozone bleaching softwood kraft pulp and acid-washed softwood kraft pulp.



The benefits noted for acid pretreating a hardwood kraft prior to ozone bleaching were also observed for chlorine dioxide as shown in Figure 12. In summary, the bleaching results from Figures 10-12 confirm the hypothesis that hexenuronic acids play an important role in consuming electrophilic bleaching agents such as ozone and chlorine dioxide. Removal and/or modification of hexenuronic acids prior to bleaching could result in substantial savings in bleaching chemical costs.

Figure 12: Chlorine dioxide bleaching hardwood kraft pulp and acid-washed softwood kraft pulp.



Note: 0.61% charge of ClO_2 employed

Goals 2 & 3: (2) Develop an experimental method to directly quantify hexenuronic acids in pulp.

(3) Determine if the hexenuronic acid content of kraft pulps can be influenced by AQ or polysulfide pulping technologies.

Following these initial investigations, the Fall 1996 PAC Review recommended that research efforts be directed toward developing a direct method of analyzing the hexenuronic acid content of kraft pulps. The method we selected was a UV-procedure developed by Vuorinen et al. (Conf. Proceedings from 1996 Int. Pulp Bleaching Conf., 1, p 43, 1996). This method employs acid hydrolysis conditions to release the hexenuronic acids from the pulp (rxn conditions: pH 3.5: 8 mM formic acid + 2 mM sodium formate, 110°C, 1 h) and subsequently convert them into 2-furoic acid and 5-carboxy-2-furaldehyde (see Fig. 2). The presence of these two compounds in the acid effluents can be readily monitored by UV, and the concentration of hexenuronic acids can be correlated to 2-furoic acid. A series of hardwood kraft pulps, described in Table 1, were employed to develop the UV analysis method. Each pulp in Table 1 was treated under pressurized acidic hydrolysis conditions, and the effluents were analyzed for furoic acid, and the kappa number of the hydrolyzed pulps was also determined. The results of these analysis are presented in Table 2 and Figures 13 - 15.

Table 1: Hardwood kraft pulps employed for hexenuronic acid studies in sections 2 and 3.

Pulp	Kappa #	% AQ	%EA
Industrial pre-O2	15.7	--	--
Industrial post-O2	10.6	--	--
lab	47.0	--	13
lab-AQ	43.2	0.050	13
lab-AQ	38.4	0.100	13
lab-AQ	36.0	0.025	14
lab-AQ	33.5	0.075	14
lab	32.1	0	15
lab-AQ	27.3	0.050	15
lab	24.3	0	17
lab-AQ	24.3	0.025	16
lab-AQ	22.4	0.050	17
lab-AQ	20.2	0.100	17

Note: Pulps were provided to P.I. High kappa pulps provided an opportunity to compare hexenuronic acid content of kappa 30 pulps from hardwood and softwood.

Analysis of the results noted for the low kappa pulps (see Table 2) and for the high kappa pulps (see Figure 13 - 15) clearly indicates a difference in the contribution of the hexenuronic acids present. Presumably the different cooking conditions employed to acquire these pulps influence the content of hexenuronic acids. The results from the high kappa pulps (Figures 13 and 14) suggest that the generation of hexenuronic acids is not a simply linear relationship. Furthermore, our data suggest that a substantial increase in hexenuronic acids may be occurring as the kappa number of the hardwood pulps is reduced below a value of twenty (i.e., compare data in Figures 4 and 14). Alternatively, the results shown in Figures 13 and 14 could be due to an anomalous hardwood pulp that simply does not follow the trends noted in Figure 4. It is interesting to note that the AQ pulps appear to have a higher level of hexenuronic acids (see Fig. 13), although additional studies will be required to determine if this value is statistically valid.

Table 2: Changes in kappa number and concentration of 2-furoic acid in the effluents of industrial hardwood kraft pulps treated with pressurized acid: pH 3.5,110°C, 1 h.

Starting Pulp	Kappa # of pulp before & after acid treatment	Concentration of 2-furoic (mmol/kg pulp)
Commercial pre-O_2	15.7 - 7.9	7.30
Commercial post-O_2	10.6 - 4.2	5.11

Figure 13. Concentration of 2-furoic acid in effluents from treating lab HW kraft pulps with pressured formic acid: pH 3.5,110°C, 1 h.

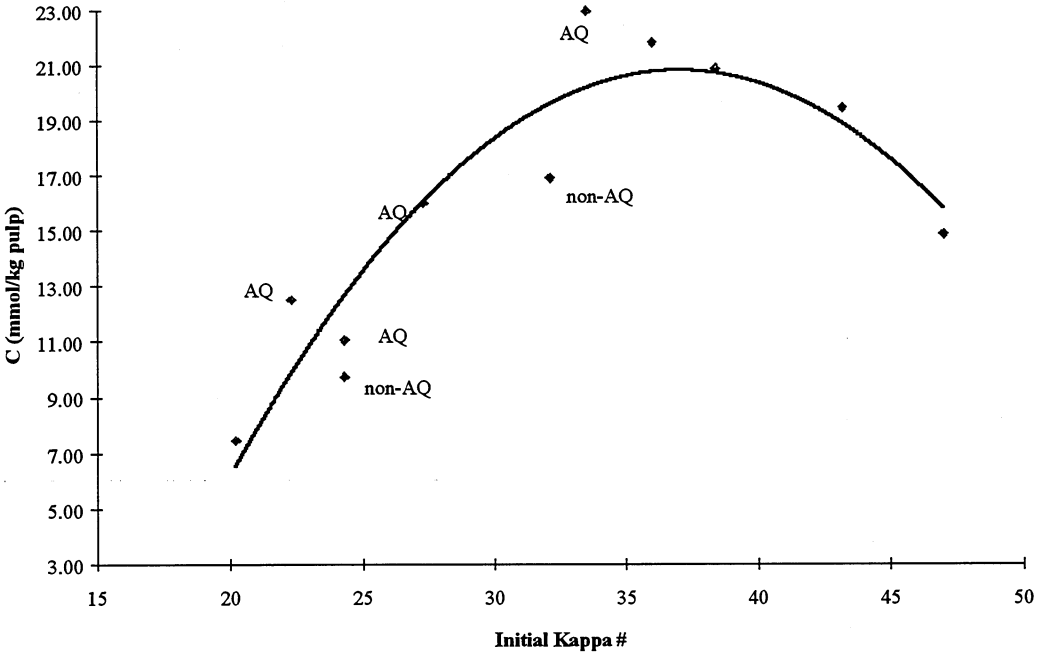


Figure 14: Change in kappa number for hardwood lab pulps treated under pressurized acidic conditions: pH 3.5,110°C, 1 h.

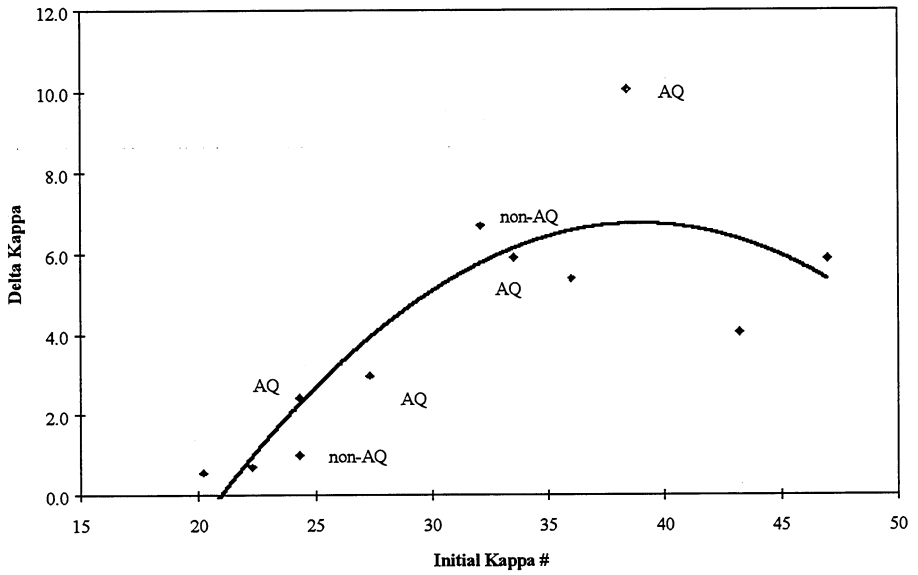
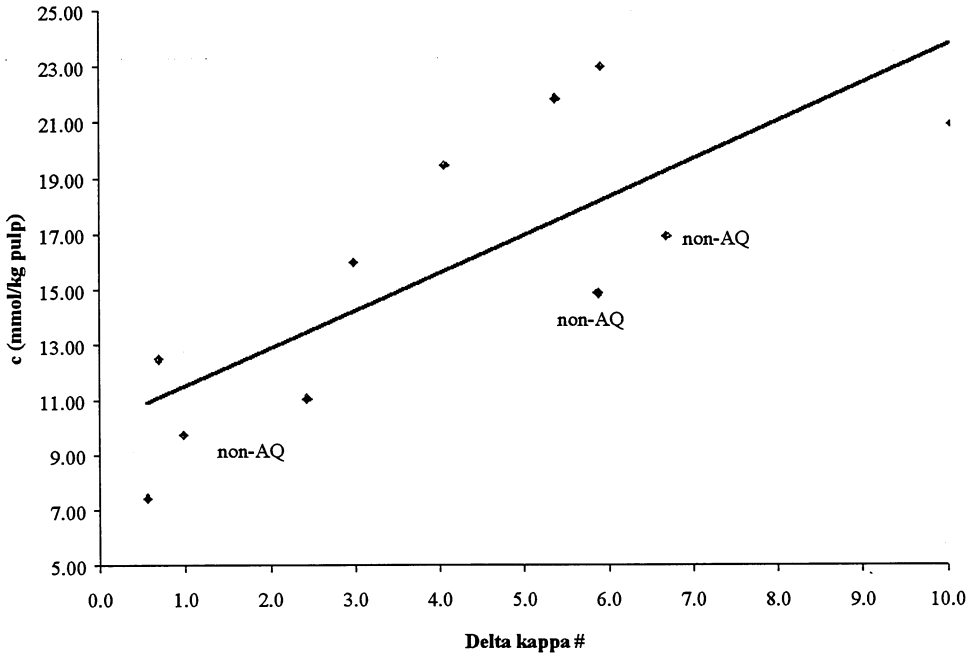


Figure 15: Correlation between generation of 2-furoic acid and change in kappa number upon treatment of high-kappa hardwood pulps.



In addition to these studies, it was requested by PAC that the metals profiles of the pulps be determined before and after the pressurized acid is performed. The results of the metals analysis of the starting and acid-treated kraft pulps are summarized in Table 3. As anticipated the pressurized acid treatment significantly decreased the metals content of the pulps examined.

Table 3: Changes in metal content of kraft pulps treated under pressurized acid conditions: pH 3.5,110°C, 1 h.

	Metals in Hardwood Kraft Fibers Determined by ICP Emission Spectroscopy First entry/pulp is metals content (mg/kg) prior acid treatment Second entry/pulp is metals content (mg/kg) post acid treatment							
Pulp ID[1] (kappa #)	Cr	Mn	Fe	Ni	Al	Na	Mg	Ca
lab (47.0)	8.63 8.53	70.8 13.8	40.5 32.9	4.70 4.21	8.91 8.24	1460 66.7	394 72.1	2670-before 553-after
lab-AQ (43.2)	13.6 12.8	59.7 12.1	37.2 32.0	5.62 2.96	7.47 9.13	1670 133	376 69.2	2430-before 518-after
lab-AQ (38.4)	11.3 10.4	67.4 13.3	46.6 20.8	4.54 1.88	13.5 8.85	1120 53.6	419 72.5	2550-before 507-after
lab-AQ (36.0)	14.4 12.6	61.6 8.36	37.2 21.6	5.03 2.38	7.45 9.95	708 34.8	403 48.2	2560-before 358-after
lab-AQ (33.5)	12.5 12.2	55.6 8.05	41.6 26.1	5.56 2.93	8.39 8.10	1140 71.9	349 44.3	2300-before 336-after
lab (32.1)	14.7 14.7	57.3 7.17	41.3 20.3	6.11 2.49	8.31 7.35	751 32.0	371 40.7	2400-before 310-after
lab-AQ (27.3)	16.1 15.4	61.5 8.43	63.8 48.4	7.36 2.75	8.76 8.36	855 41.0	357 43.3	2220-before 310-after
lab (24.3)	16.0 14.4	57.4 6.47	45.2 27.4	6.88 2.82	12.8 9.19	422 20.8	378 37.4	2170-before 252-after
lab-AQ (24.3)	14.5 13.1	60.2 7.58	34.0 18.8	6.23 1.91	9.21 8.35	1010 44.2	336 39.6	2070-before 272-after
lab-AQ (22.4)	12.5 11.7	57.6 5.78	32.7 16.5	5.27 1.64	7.88 7.67	504 28.7	330 29.8	2040-before 223-after
lab-AQ (20.2)	17.1 13.6	56.9 5.64	42.8 22.3	5.59 1.76	10.8 6.45	548 24.1	355 31.6	3390-before 233-after
Industr. pre-O2 (13.3)	1.65	90.2	<.40	1.25	15.9	155	380	2950-before
Industr. post-O2 (10.6)	0.51 0.86	66.6 14.7	7.94 9.91	<.54 1.69	11.6 11.2	1500 431	187 36.5	2590-before 671-after

[1]see Table 1 for further description of pulps

Experimental:

Materials: Commercial softwood and hardwood kraft pulps were acquired from several pulping mills throughout North America. Laboratory softwood kraft pulps described in Figure 6 was prepared under simulated EMCC® pulping

conditions, and the laboratory pulps in Table 1 were prepared in a modified M&K digester under conventional conditions.

Acid Hydrolysis:
Refluxing: A 3% consistency solution of well-washed kraft pulp, 8.0 mM formic acid, and 2.0 mM sodium formate was refluxed. Pulp aliquots were removed, washed, and analyzed for kappa number.

Pressurized: A 3% consistency solution of well-washed kraft pulp, 8.0 mM formic acid, and 2.0 mM sodium formate was placed in a pressure vessel and heated to 110°C for 1 h. The pulp was then analyzed for metals content and kappa number. The acid effluents were analyzed by UV for 2-furoic acid the following Vuorinen procedure (Conf. Proceedings from 1996 Int. Pulp Bleaching Conf., 1, p43, 1996).

Analytical Methods: Kappa number and viscosity determinations were performed following TAPPI standard procedures. Metals analysis was determined by ICP emission spectroscopy.

Future Recommendations:
Having established the relevancy of hexenuronic acids to hardwood kraft bleaching operations and adopted a quick analytical tool to detect these unsaturated sugars, several research opportunities are available, including:
Control of Hexenuronic Acids (HA) During Pulping:

- Determine the rate of (HA) formation during pulping;
- Determine the Influence of polysulfide on HA formation.

Bleaching Chemistry of Hexenuronic Acids:

- reactions of HA with ozone;
  - formation of oxalic acid;
- reactions of HA with ClO_2;
  - AOX formation.

The goal of these proposed studies would be to develop the fundamental knowledge about hexenuronic acids so that their formation and/or bleaching impact could be minimized.

Research Benefits:
The anticipated benefits of these studies include:

- reduced bleaching costs;
- reduced generation of oxalic acid, facilitating mill closure;
- improved mill operations.

FUNDAMENTALS OF BLEACHING CHEMISTRY

Biobleaching Studies - Laccase

Laccase-Mediator Bleaching of Kraft Pulps *by Art J. Ragauskas*

Executive Summary

The long-term research goal of this project is to develop new methods of improving kraft bleaching operations employing enzymatic technologies. Over the past two years, our research studies have focused primarily on laccase. This year's research studies were directed at understanding the biobleaching chemistry of laccase and N-hydroxybenzotriazole (LM-stage). As an initial goal of this project, research efforts were directed toward establishing the chemical fate of N-hydroxybenzotriazaole. Preliminary studies demonstrated that LM bleached kraft pulps were enriched in nitrogen when analyzed by elemental analysis. Caustic extraction was found to remove some of these nitrogen-containing materials, but not all of this extraneous material could be extracted. Although we were unable to definitely establish if the nitrogen in the pulp was due to the mediator and/or the laccase, we were able to determine that 99% of the mediator material could be recovered, suggesting that the incorporation of nitrogen into the pulp was due to the enzyme. A structural reactivity relationship of N-hydroxybenzotriazole demonstrated that it was absolutely critical for the hydroxy group of the mediator to be directly attached to N-1 of the triazole ring. Furthermore, we observed that the placement of electron-withdrawing groups on the aromatic ring was detrimental toward the biobleaching effect. Attachment of an electron-donating group onto the aromatic ring of the mediator also decreased the delignification capabilities of the LM-stage.

The influence of varying the methoxy content of the pulps was explored during this fiscal year by preparing a series of pulps with varying amounts of methoxy content. The behavior of these pulps in a LM-stage was explored, and our preliminary investigations suggested that a high methoxy content kraft pulp could be detrimental to LM delignification.

Introduction

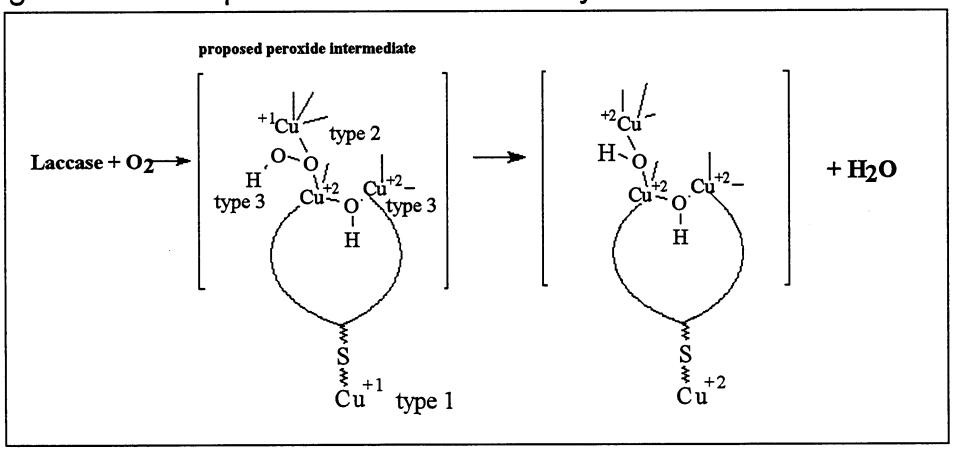
The 1996 Spring PAC Review identified the bleaching chemistry of a laccase/N-hydroxybenzotriazole stage as a research area of high interest. This report will briefly review the past research efforts in this field and summarize recent studies in Ragauskas' laboratory.

Literature Overview

Laccase (EC 1.10.3.2) is a multiform, extracellular oxidase that catalyzes a four-electron reduction of dioxygen to water with a concomitant oxidation of various organic substrates [(a) Solomon, E.I.; Baldwin, M.J.; Lowery, M.D., Chem. Rev., 92, 521(1992); (b) Solomon, E.I.; Lowery, M.D., Science, 259, 1575(1993)]. The active site of the enzyme contains four copper ions, constituting three different oxidation-reduction sites, all of which are essential for the catalytic active of this

enzyme [Cole, J.L.; Clark, P.A.; Solomon, E.I., J. Am. Chem. Soc., 112, 9534(1990)]. Fee and Malmstrom [Biochim. Biophys. Acta, 153, 229(1968)] have reported that the redox potential for the three types of copper (Note: frequently referred to as type, 1, 2, & 3) atoms in laccase is approximately +400 mV. The active site of laccase has been studied in detail, and it has been shown that the type 2 and 3 centers function as a trinuclear copper complex with respect to oxygen and other ligands [Spira-Solomon, D.J.; Allendorf, M.D.; Solomon, E.I., J. Am. Chem. Soc., 108, 5318(1986); (b) Cole, J.L.; Tan, G.O.; Yang, E.K.; Hodgson, K.O.; Solomon, E.I., J. Am. Chem. Soc., 112, 2243.]. Solomon has extensively studied the redox chemistry of laccase and has suggested that the type 2 and 3 copper sites form a peroxide-copper complex upon binding oxygen at the active site [Shin, W.; Sundaam, U.M.; Cole, J.L.; Zang, H.H.; Hedman, B.; Hodgson, K.O.; Solomon, E.I., J. Am. Chem. Soc., 118, 3202(1996)]; the proposed peroxide structure is shown in Figure 1.

Figure 1: Proposed active-site chemistry of laccase.

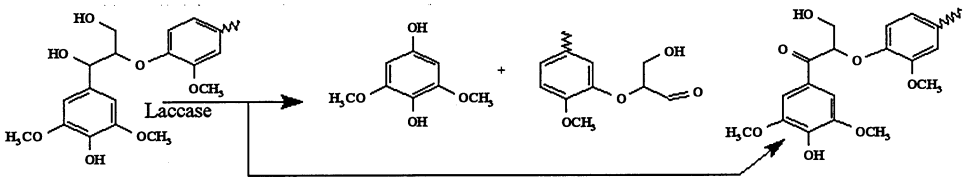


The peroxy-copper complex is then further reduced by type 1 and type 2 copper, yielding a molecule of water. The oxidized copper species can then be reduced by an exogenous substrate. The oxidative properties of these copper atoms become the key function components involved in oxidizing lignin and future biobleaching technologies.

Bleaching Chemistry of Laccase

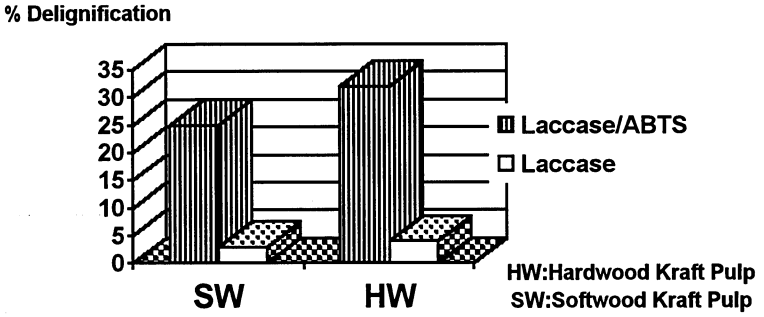
It has been known for several decades that white-rot fungi utilize lignin peroxidase, manganese-peroxidase, and laccase in the course of extracellular lignin degradation of wood [Boyle, C.D.; Kropp, B.R.; Reid, I.D., App. Environ. Microbiol., 58(10), 3217(1992)]. Hence, the reactions of laccase with lignin and lignin model compounds have been extensively studied [Higuchi, T., Wood Sci. Technol., 24, 23(1990)]. and Figure 2 illustrates typical laccase catalyzed degradation reactions of lignin. Despite the rather efficient degradation of lignin by laccase, the utilization of this enzyme during pulp bleaching is not feasible because the enzyme cannot rapidly diffuse into a pulp fiber, where most of the residual lignin is located.

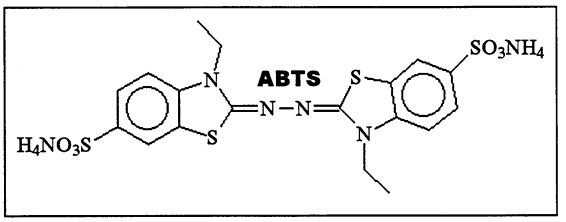
Fig. 2: Proposed laccase degradation reactions of lignin structures



The first, true breakthrough in this field came about by Bourbonnais and Paice [Appl. Microbiol. Biotechnol., 36, 823(1992] when they demonstrated that the addition of ABTS (2,2'azino-bis(3-ethylbenzthiazoline-6-sulphonic acid) could lead to substantial delignification of kraft pulps after an alkaline extraction stage, as summarized in Figure 3.

Fig. 3: Delignification of Kraft Pulps by Laccase & ABTS

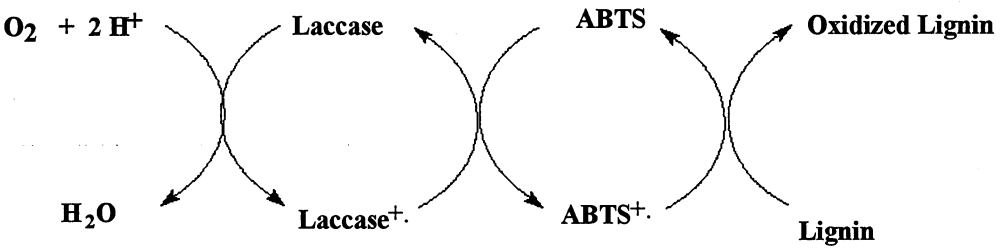




The difficulties of utilizing this system for bleaching purposes are three-fold: (i) the extent of delignification is not sufficient; (ii) bleaching times are too long; and (iii) the mediator is too complex and too expensive to permit commercialization. Nonetheless, this development was a significant advancement, and it initiated a flurry of fundamental research studies into the mechanism of laccase/ABTS bleaching [Bourbonnais, R.; Paice, M.G., FEBS Lett., 267, 99(1990)]. The results of these studies lead to the suggestion that the mechanism of delignification for laccase/ABTS is based on a series of connective oxidative reactions as summarized in Figure 4. The exact role of ABTS in the delignification process remains controversial as Potthast et al. [Potthast, A.; Rosenau, T.; Chen, C.-L.; Gratzl,

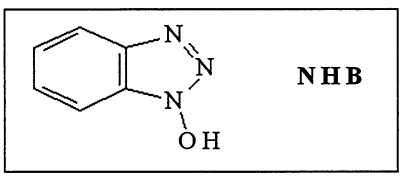
J.S., J. Org. Chem., 60, 4320(1995)] and Muheim et al. [Muheim, A.; Fiechter, A.; Harvey, P.J.; Choemaker, H.E., Holzforschung, 46, 121(1992)] have suggested that the laccase-ABTS system does not generate a radical cation. Potthast has suggested that ABTS acts instead, as a single-electron donor to laccase and activates the enzyme but does not function as an oxidant, at least not for the oxidation of low molecular weight compounds.

Figure 4: Proposed Laccase/ABTS Delignification Mechanism



Based on the results of these fundamental studies, Call identified a new mediator, N-hydroxy-benzotriazole (NHB), that illustrated the potential commercial viability for a laccase-based bleaching system [Call, H.P., World patent application: WO 94/29510]. Figure 5 provides a comparative illustration of the bleaching capabilities of ABTS and NHB with laccase, followed by an alkaline extraction stage.

Fig. 5: Delignification of a Softwood Kraft Pulp by Laccase, ABTS, & NHB



Since this initial discovery, Call has demonstrated the applicability of the laccase/N-hydroxybenzotriazole bleaching system with numerous softwood and hardwood

chemical pulps, further optimized the laccase/NHB system (Note: currently, 5 kg of NHB are employed/ton of air dry pulp), and verified laboratory results with pilot-plant trials [Call, H.P.; Mucke, I., Non-Chlorine Bleaching Conference Proceedings, Amelia, FL (1995)]. Despite these significant advances, further improvements will be needed prior to commercialization of this process, including:

- Increased delignification with a laccase/mediator system;
- Simplified mediator requirements;
- Non-enzymatic based technologies.

Research studies in F015 are directed at solving these long-term challenges.

Research Goals

The FY 1996-97 goals for this section of F015 are listed below:

1. Determine the fate of N-hydroxybenzotriazole after laccase-mediator bleaching protocol.

2. Study the biobleaching efficiency of an electron-rich and electron-poor benzotriazole derivative with laccase.

3. Examine the biobleachability of kraft pulps with varying levels of methoxy content employing the laccase-mediator bleaching system.

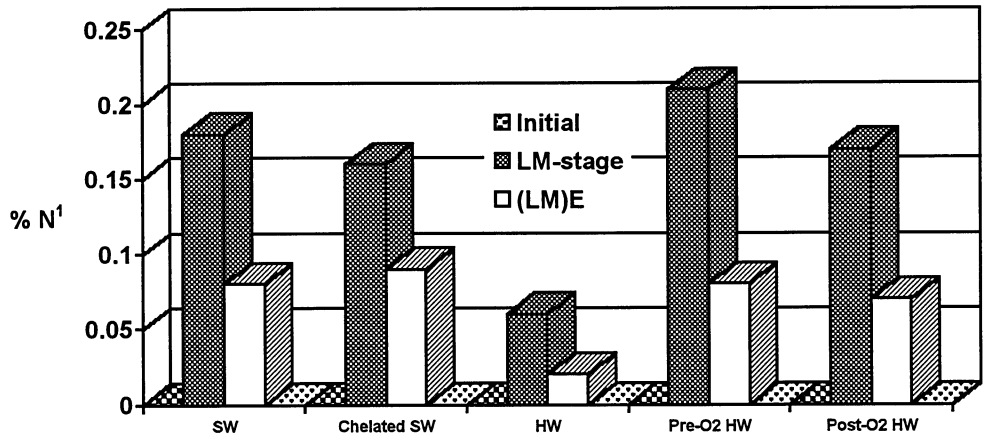
These research goals have been accomplished over this past fiscal year, and the results of these investigations are summarized in this report.

Results

Goal 1: Fate of N-hydroxybenzotriazole during LM-stage.

Research studies from the previous fiscal year had established that LM bleached pulps were enriched in non-extractable nitrogen (see Fig. 6). Unfortunately, it was not possible to determine if this nitrogen was originating from the laccase or if it was due to the mediator.

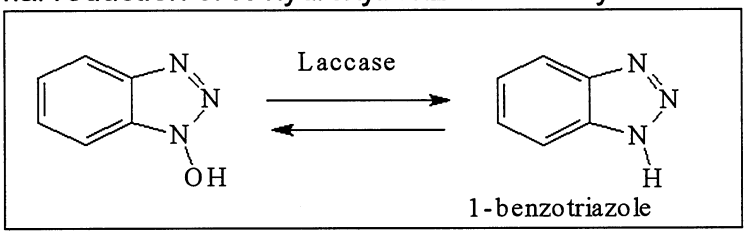
Figure 6: Non-extractable nitrogen present in brownstock, after LM-stage, and after (LM)E treatment.



[1]determined by elemental analysis

To explore the fate of the mediator during bleaching, a southern softwood kraft pulp was treated with laccase under our standard LM-conditions. The starting kappa number of the pulp was 25.1 and after the LM-stage 20% delignification was achieved. (Note: Past experience suggests that an additional 20% delignification could have been achieved if the pulp would have been extracted under caustic conditions.) The LM-treated pulp was then filtered, washed extensively with water, and then air-dried. The dry pulp was then soxhlet extracted with acetone for 24 hrs, and the extracts were concentrated under reduced pressure, yielding 0.034 gr of mediator material. The LM bleach effluents were filtered and freeze dried, yielding an additional 0.065 gr of mediator material. Preliminary NMR analysis of the pulp extracts and bleach effluents indicated the presence of two species that were structurally related. The identities of these two compounds were readily established as starting material and 1-benzotriazole (see Fig. 7). This previously unreported rearrangement was confirmed by advanced NMR and MS-studies. Studies performed by Sealey (IPST Ph.D. student) have demonstrated that this conversion occurs only in the presence of laccase, and the reduced product is inactive with respect to the LM-system.

Figure 7: Formal reduction of N-hydroxybenzotriazole by laccase.

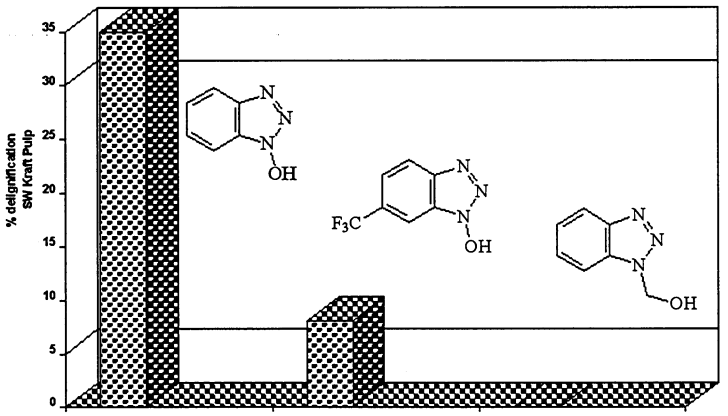


In summary, mediator recovery was greater than 99% (on a mole basis), suggesting that nitrogen incorporation into pulp during a LM-stage is occurring due to the enzyme. Of greater significance is the detection of a 1-benzotriazole in the LM-stage. This inactive form of the mediator suggests that the efficiency of a LM-stage could be improved if the stability of the mediator could be improved.

Goal 2: Structural mediator requirements for efficient LM delignification.

This goal was accomplished by employing a series of modified N-hydroxybenzotriazole mediators for LM-bleaching. The mediators examined and the results of the laccase-mediator bleaching procedure are summarized in Figure 8.

Figure 8: Use of modified N-hydroxybenzotriazole mediators for laccase biobleaching of a softwood kraft pulps starting kappa # 25.1.



Based on the results shown in Figure 8, it is clear that the hydroxy group of N-hydroxybenzotriazole must be attached to the nitrogen. Furthermore, the placement of an electron-withdrawing group on the aromatic ring of 1-hydroxybenzotriazole (see Fig. 8, 1-hydroxy-6-(trifluormethyl)benzotriazole) is detrimental to the performance of the mediator. Subsequent studies by Sealey indicated that the replacement of the CF_3 group of 1-hydroxy-6-(trifluormethyl)-

benzotriazole with an electron-donating group such as CH_3 or OCH_3 is also detrimental to the performance of the LM-bleaching system. These results suggest that the mediator, 1-hydroxybenzotriazole, plays a very specific role in the overall LM-bleaching process, and the chemistry of this mediator has yet to be fully determined.

Goal 3: **Laccase bleaching kraft pulps with varied methoxy content.**
The final research goal for this section of F015 was to examine the reactivity of a kraft pulp that had its methoxy content systematically altered. This was attempted by methylating a softwood kraft pulp with dimethylsulfate and sodium hydroxide. The methylated pulps were then analyzed for methoxy content, bleached with the LM-system, and extracted with caustic. The results of these investigations are summarized in Table 1.

Table 1: LM-bleaching of methylated softwood kraft pulp.

Pulp	Starting Kappa #	LM	(LM)E	Δ kappa[1]	Methoxy Content (% wt)	Δ TAPPI brightness [2]
Brownstock	30.8	23.8	20.8	10.0	1.18	1
½charge methylated-pulp[3]	26.7	20.8	17.7	9.6	--	7
Methylated pulp[4]	23.6	17.5	15.1	8.5	1.20	11
Double methylated pulp[5]	22.2	16.5	14.7	7.5	1.43	11

[1]change in kappa number before initial laccase treatment and after caustic extraction;[2]change in Tappi brightness before initial laccase treatment and after caustic extraction;[3]pulp methylated with 1.00 gr dimethylsulfate/1.00 gr od pulp, see experimental section for further detail;[4]pulp methylated with 1.95 gr dimethylsulfate/1.00 gr od pulp see experimental section for further detail; [5]pulp methylated with 3.80 gr dimethylsulfate/1.00 gr od pulp twice, see experimental section for further detail.

Data analysis of the LM-bleaching stage was complicated by the fact that the methylation procedure appeared to extract substantial amounts of lignin from the pulp. Hence, although the extent of delignification by a LM-stage is decreased for the methylated pulps, the magnitude of this reduction is at best only 25%. These results tend to suggest that the LM-stage is not overly dependent on free phenolic structures for delignification, although further experimentation is needed to confirm this.

Experimental

Materials: Commercial softwood kraft pulps were acquired from several pulping mills in the US. All chemicals were purchased from commercial vendors

and used as received. Laccase, isolated from a Polyporus fungi, was provided by Novo Nordisk. The enzyme was frozen to -20°C until use. Once thawed, the activity of the enzyme was measured, and the proper dose was added to the pulp.

Methods

Laccase assay: The activity of the laccase was measured by monitoring the rate of oxidation of syringaldazine. The change in A_{530nm} of 0.001 per minute per mL of enzyme solution in a 100 mM potassium phosphate buffer (2.2 mL) and 0.216 mM syringaldazine in methanol (0.3 mL) was set to one Unit of activity. This test was performed at 23°C.

General laccase/mediator biobleaching stage (LM-stage): The biobleaching trials were performed in a pressurized vessel with 10 bar (145 psi) O_2 pressure for 24 hrs at 45°C. Typically 10 gr at 10% consistency were added to the preheated pressure vessel, and the mediator (0.0015 mols/gr od pulp) was added and stirred for 3 min. The pH was then adjusted to 4.5, and the enzyme solution (1.75×10^6 Units activity/gr od pulp) was added (pH remained ~ 4.5). After treatment, the mixture was filtered, and an alkali extraction was performed with a 2% NaOH charge for 1 hr at 70°C.

Pulp Methylation: Softwood kraft pulps were methylated following the procedure developed by Francis and Reeve (J. Pulp Paper Sci., 13(6), J171 1987). The ½ charge methylated pulp employed 1.00 gr dimethylsulfate/gr of od pulp. The methylated pulp employed 1.90 gr dimethylsulfate/gr of od pulp and the double methylated pulp was re-methylated a second time under the latter conditions.

Analytical Methods: Kappa number and viscosity determinations were performed following TAPPI standard procedures. Metals analysis was determined by ICP emission spectroscopy.

Future Recommendations

Proposed research studies are targeted at further defining the mechanism by which the LM-stage oxidizes lignin and examining the use of laccase as a convenient, low-cost technology to lower AOX. Proposed FY 1997-98 research goals include:

Chemistry of Laccase-Mediator (LM) bleaching stage:

- LM bleach a series of kraft pulps with differing methoxy contents but with comparable lignin contents;
- Characterize LM bleach effluents for methanol content.

Use of laccase for in-situ AOX destruction:

- reactions of laccase with Do effluents;
- reactions of laccase with effluents from DoE* E*:E, EO, or EOP.

Research Benefits

The anticipated benefits of these studies include:

- New low-capital, bleaching technology;
- AOX destruction.

Related Student Studies:

Fundamental Investigations Into Oxidoreductase Enzymatic Bleaching Systems, J. Sealey, *IPST Ph.D. Student*

The use of biological processes for bleaching of chemical pulp has studied for many years with little to no success. Until recently the use of fungi, that excrete extracellular enzymes or isolated enzymes have been ineffective in delignifing kraft pulps. A promising new process that incorporates laccase with a mediator has been reported. The purpose of this study is to provide fundamental information on the mechanism of the laccase-mediator biobleaching system. This study is divided into three phases. The first phase examined the reaction between the lignin in pulp and the laccase mediator mixture; The second phase determined the reaction between the mediator and laccase; and the final phase will examine the reaction between isolated lignin and laccase (with and without the mediator). This information, along with a prescreening of active mediator structures, will be used to determine the limiting factors in delignification and provide fundamental mechanistic information that can be used to improve the effectiveness of the laccase-mediator biobleaching process.

Fiber Modification by Laccase, *K. Haynes, IPST Ph.D. Student*

Recent research has shown that the laccase mediator delignification system introduces carboxylic acid groups to the residual lignin in pulp fibers. The presence of carboxylic acid groups on a fiber has many beneficial properties for papermaking. This project will identify the effects of a laccase mediator delignification system on fiber properties. A comparison will be made between the enzymatic system and the use of oxygen delignification.

In the second phase of this research, studies will explore the use of enzymatic delignification processes to introduce carboxylic acid groups onto a variety of fiber grades including linerboard and semi-bleached kraft pulp. The amounts and location of carboxylic acid groups introduced enzymatically into pulp will be fully established. The impact of these modifications on papermaking properties will be determined.

This research is expected to increase our understanding of laccase mediator delignification, and the role of surface carboxylic acid groups in the development of specific bond strength.

ATTACHEMENT # 1

Residual lignin studies of laccase delignified kraft pulps

J. Sealey and A.J. Ragauskas
submitted to J. Enzyme and Microbial Technology

Residual lignin studies of laccase delignified kraft pulps

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Keywords: Laccase, biobleaching, delignification, lignin

Introduction

The removal of lignin from wood is a key operation in the manufacturing of high-value paper products. Although most lignin is removed from wood during pulping, the last vestiges must be removed using a series of oxidation bleaching reactions. Historically, this was accomplished using hypochlorous acid or chlorine.[1] Recently, environmental concerns have lead to the development of alternative bleaching agents, including chlorine dioxide, ozone, and hydrogen peroxide.[2] The enormous potential of applying biological treatments to displace chemical bleaching stages has not been ignored, and several research groups have been active in this field. Until recently, few biological treatments could claim to have the bleaching efficiency of chemical agents. Call's recent patent of laccase and N-hydroxybenzotriazole as an efficient bleaching stage has dramatically altered the near-term bleaching potential of biological-based bleaching technologies.[3]

The role of laccase in biological systems to catalyze the polymerization and depolymerization of lignin has been extensively investigated.[4] The use of laccase to delignify kraft pulps has been historically limited since the enzyme can not diffuse into the fibers due to size limitations.[5] Attempts to circumvent these limitations have focused on the use of chemical mediators, which are believed to be oxidized by the enzyme and then undergo oxidative reactions with lignin in the pulp fiber. Prior to Call's patent, the best available mediator was 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid), which was shown to delignify kraft pulps by 27% over a period of 4 hours.[6] In comparison, the use of laccase and N-hydroxybenzotriazole leads to 50-60% delignification of kraft pulps over a period of 4 hours.[7] Control experiments demonstrated the need for both the mediator and laccase to be present in the reaction vessel during the biobleaching process.[7] Call has demonstrated that pulps biobleached with laccase/N-hydroxybenzotriazole can be readily bleached to high brightness values and that this methodology could be incorporated into modern bleaching practices.[8]

Our own research group has been active in applying biotechnology to the field of pulp and paper,[9] and we have recently begun to investigate the fundamental principles involved in the laccase/N-hydroxybenzotriazole bleaching system. This paper presents some of the first reported results summarizing the effects of laccase and N-hydroxy-benzotriazole on the structure of residual lignin during biobleaching.

Materials and Methods

Materials

N-hydroxybenzotriazole, p-dioxane, 1.0 N HCl, pyridine, and deuterochloroform were commercially purchased and used as received.

Bleaching studies employed two industrial, never-dried, softwood kraft pulps. The first pulp (pre-O_2) sample was collected after continuous, extended kraft delignification, and the second was acquired after oxygen delignification of pulp 1 (post-O_2). Physical properties for both pulps are summarized in Table 1. Prior to using the pulps for the studies reported in this paper, the extractives were removed following TAPPI method T-264.[10] The extractives were removed from the pulp to simplify subsequent lignin characterization studies.

Laccase, isolated from a Polyporus fungi, was provided by Novo Nordisk. The enzyme was frozen to -20°C until use. Once thawed, the activity of the enzyme was measured, and the proper dose was added to the pulp.

Methods

Laccase assay. The activity of the laccase was measured by monitoring the rate of oxidation of syringaldazine. The change in A_{530nm} of 0.001 per minute per mL of enzyme solution in a 100 mM potassium phosphate buffer (2.2 mL) and 0.216 mM syringaldazine in methanol (0.3 mL) was set to one Unit of activity. This test was performed at 23°C.

General laccase/N-hydroxybenzotriazole biobleaching stage (LMS stage). The biobleaching trials were performed in a pressurized vessel with 10 bar (145 psi) O_2 pressure for 24 hrs at 45°C. The pulp was added to the preheated vessel, and the mediator was added and stirred for 3 min. The pH was then adjusted to 4.5, and the enzyme solution was added (pH remained ~ 4.5). After treatment, the mixture was filtered, and an alkali extraction was performed with a 2% NaOH charge for 1 hr at 70°C.

Physical and chemical characterization of kraft pulps. The lignin content of the kraft pulps was determined by $KMnO_4$ titration of the pulp following standard TAPPI method T-236 and expressed as a "kappa number." This value is an indirect measurement of lignin content: % lignin content=0.147 x kappa number. The viscosity of the pulp was measured employing a capillary viscometer as described in TAPPI method T-230.[10]

General lignin isolation procedure. Air-dried pulps were extracted with a 9:1 dioxane/aqueous acid solution (0.1 N HCl). The extraction was performed at 4% consistency and refluxed for 2 hrs under an argon atmosphere. The mixture was then filtered, and the filtrate was filtered through celite. The solution was neutralized and concentrated under reduced pressure. After the volume was reduced to less than 10% of the original volume, 200 mL of distilled water was added three separate times and

reconcentrated. The lignin solution was then acid precipitated by lowering the pH to 2.5 with HCl. The acid-precipitated lignin was then washed several times with distilled water and freeze-dried. The yield of lignin for this process averaged between 55-40 % (lignin yield=[mass lignin isolated/lignin present in pulp, calculated from the kappa #]%)

Lignin NMR studies. NMR spectra data were acquired with a DMX 400 MHz Bruker spectrometer. Quantitative ^{13}C-NMR experiments were performed following standard literature methods.[11] In brief, 100 mg of residual lignin was dissolved into ca. 0.6 ml of DMSO-d_6 and filtered into a 5-mm NMR tube. All spectra were recorded at 50°C. Typical recording conditions employed a 90° pulse, 11 sec pulse delay, 25,000 Hz sweep width with an inverse gated decoupling pulse sequence requiring approximately 15,000 transients for acceptable signal-to-noise.

Results and Discussion

The effects of the laccase/N-hydroxybenzotriazole biobleaching system was initially explored with an industrial softwood kraft pulps isolated before and after oxygen delignification. In each case, the pulp was treated with a laccase mediator system for 24 hours at 45°C and 10 bar of O_2 pressure. Optimal enzyme dosage was determine by increasing the enzyme dose while holding all other reaction conditions constant (see Figure 1). A sharp decrease in kappa number was detected at 400,000 U for a 10g batch of oven dry pulp, and increasing the enzyme dosage did not increase lignin removal. Variations in the mediator dosage from 200 mg to 400 mg per 10g of oven dry pulp per 400,000 U laccase gave no increase in lignin removal for both the pre- and post-oxygen delignified kraft pulps.

As shown in Figure 1 optimal delignification results were achieved with the post-oxygen delignified kraft pulp. Table 1 summarizes the physical properties of the pulps after maximizing the biobleaching effect of the LMS-stage. The reductions in viscosity values for the biobleached pulps suggested that the laccase-mediator system was selective for lignin and did not induce significant oxidative degradation of the cellulose component of the kraft pulp fibers.

Table 1. Laccase/N-hydroxybenzotriazole delignification of kraft pulps.

Kraft Pulp	Initial		Post-bleaching	
	Lignin Content (kappa #)	Viscosity (cP)	% Delignification	% Viscosity Loss
Pre-O_2	25.5	30.7	32	20
Post-O_2	17.2	26.8	53	31

Insert Figure 1

The mechanisms contributing to the laccase/N-hydroxybenzotriazole biobleaching effect were further explored by characterizing the nature of residual lignin before and after the biobleaching/alkaline extraction stage. The residual lignin from the two starting kraft pulps were isolated employing Gellerstedt's acidic dioxane extraction procedure for kraft pulps.[12] These conditions are believed to catalyze the hydrolysis of lignin-carbohydrate bonds facilitating the dissolution of lignin into an aqueous dioxane solution. Subsequent work-up procedures provide lignin samples that were readily analyzed by FT-IR and high-field NMR. Employing the same isolation procedure for the laccase-treated, alkaline-extracted pulps yielded residual lignin samples for the pre- and post-oxygen delignified biobleached pulps. In addition to the residual lignin samples the lignin fragments present in the effluents of alkaline extracts from each laccase-treated pulp were acid precipitated, purified, and analyzed by FT-IR and NMR.

Analysis of the lignin samples by FT-IR indicated that the residual lignin from the starting pulp, post-LMS/alkaline extraction treated pulps and the alkaline effluents were structurally similar (Figure 2). The most notable change in functional groups was the increase in the relative signal intensity of the absorption centered at 1719 cm^{-1}. This signal has been assigned to unconjugated carbonyl groups present in lignin.[13]

Insert Figure 2

^{13}C NMR analysis of the residual lignin samples and alkaline effluents provided additional information on the nature of the structural changes occurring to lignin during the LMS-stage, as shown in Figure 3. All spectra data was acquired under quantitative conditions and simple integration provided a facile means of monitoring changes in functional group distribution and these results are summarized in Table 2.

Insert Figure 3

Inspection of the spectra data in Table 2 suggests that the lignin remaining in the kraft pulps after an LMS stage and alkaline extraction stage is enriched in acid groups, exhibits a small decrease in substituted guaiacyl groups and a slight enrichment of β-O-4 aryl

ether linkages. Both the pre- and post-oxygen delignified kraft pulps also appear to undergo a loss in methoxy content and a significant decrease in phenoxy content.

Table 2. Lignin functional group distribution for kraft pulps before and after biobleaching treatment as determined by quantitative ^{13}C NMR.[a]

Lignin Sample[b]	RCO_2H (δ 180.1-165.1 ppm)	C-3,4 of substituted guaiacyl units (δ 154.14-139.79ppm)	C-3,4 of guaiacyl and demethylated phenolics (δ 160.13-154.14ppm)	β-O-aryl ether Cβ (δ 89.53ppm)	CH_3O- (δ 57.39-53.88ppm)
Pre-O_2 pulp	0.44	2.2	0.39	0.38	0.84
Pre-O_2 pulp after LE	0.50	1.75	0.15	0.39	0.77
" " E-effluents	0.84	1.76	0.35	0.55	0.62
Post-O_2 pulp	0.47	2.06	0.29	0.49	0.81
Post-O_2 pulp after LE	0.56	1.79	0.24	0.53	0.57
" " E-effluents	1.05	1.72	0.33	0.54	0.66

[a]all assignments based on literature values for lignin functional groups[14]; [b] all values are relative and were determined by integrating individual spectrum, assigning the aromatic section of the spectrum (δ 160.0-106.5 ppm) a value of 6, and then measuring all other portions of the spectrum relative to this arbitrary assignment.

These results suggest that the LMS stage selectively oxidizes free phenoxy groups in lignin which are selectively removed during the alkaline extraction stage. Equally significant is the apparent unreactivity of the β-O-aryl ether linkage of lignin toward the LMS bleaching protocol. As to be expected, the alkaline effluents from LMS bleached kraft pulps (pre and post-O2) exhibited a significant increase in acid content but otherwise were comparable in structure to the residual lignin structures. Although several factors may be contributing to the chemical nature of alkaline extracts it appears that the LMS system is selective in it's oxidative degradation of lignin and does not fully oxidize all components of lignin.

Conclusions

In summary, these results demonstrate that the laccase/N-hydroxybenzotriazole bleaching system can very effectively remove lignin from kraft pulps via a series of oxidative degradation reactions. It appears the principle site of oxidative attack is the free phenoxy groups of lignin. The role of the chemical mediator, N-hydroxybenzotriazole, is key to these reactions. Further studies will be needed to fully define the mechanistic reactions that occur between laccase, N-hydroxybenzotriazole, and the lignin present in kraft pulps.

Acknowledgments

The gift of the laccase by Novo Laboratories Inc. is gratefully appreciated. Portions of this work were used by J.S. as partial fulfillment of the requirements for the Ph.D. degree at the Institute of Paper Science and Technology.

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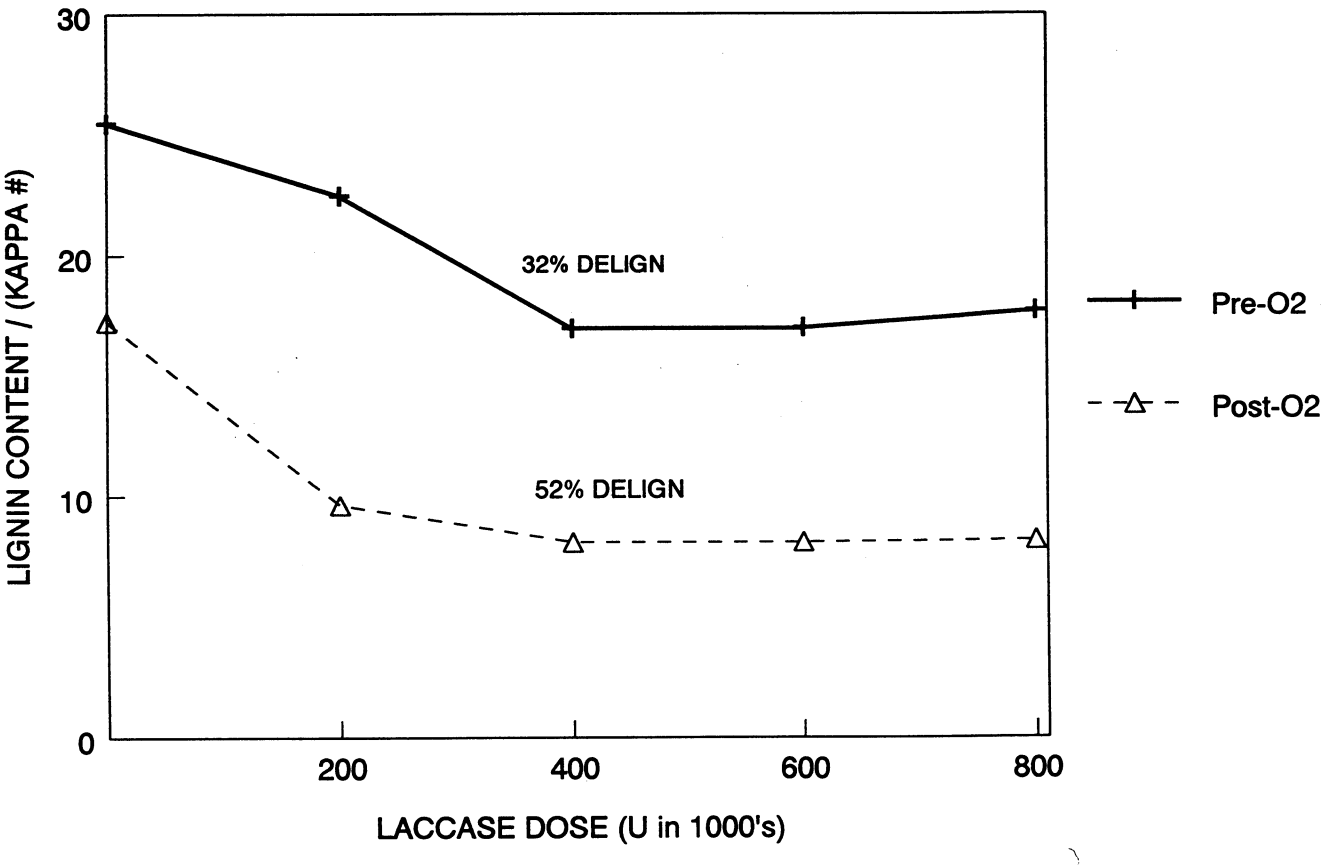
30
20
10
0
LIGNIN CONTENT / (KAPPA #)
32% DELIGN
52% DELIGN
200
400
600
800
LACCASE DOSE (U in 1000's)
Pre-O2
Post-O2

Figure 1

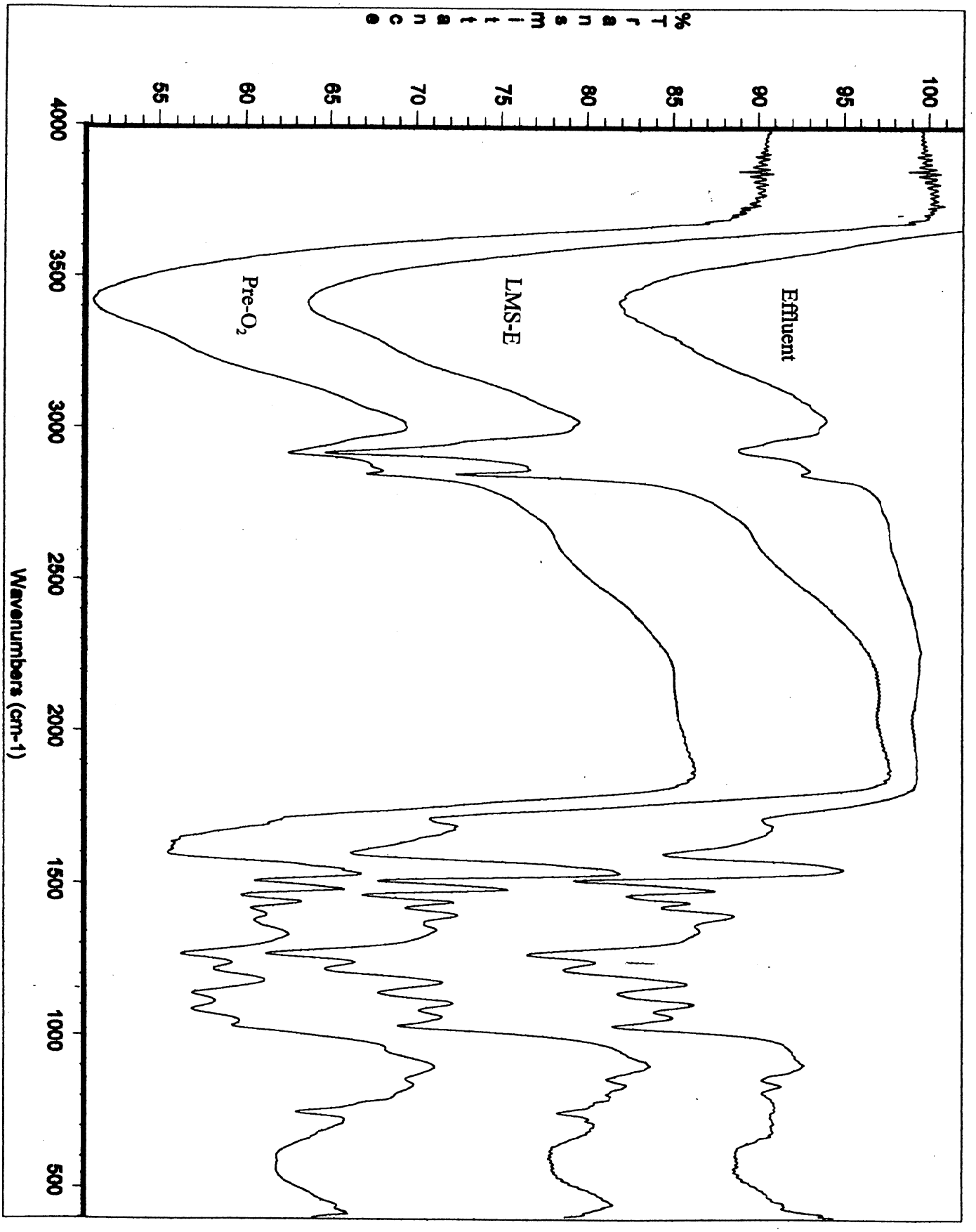
% Transmittance
100
95
90
85
80
75
70
65
60
55
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)
Effluent
LMS-E
Pre-O2

Figure 2

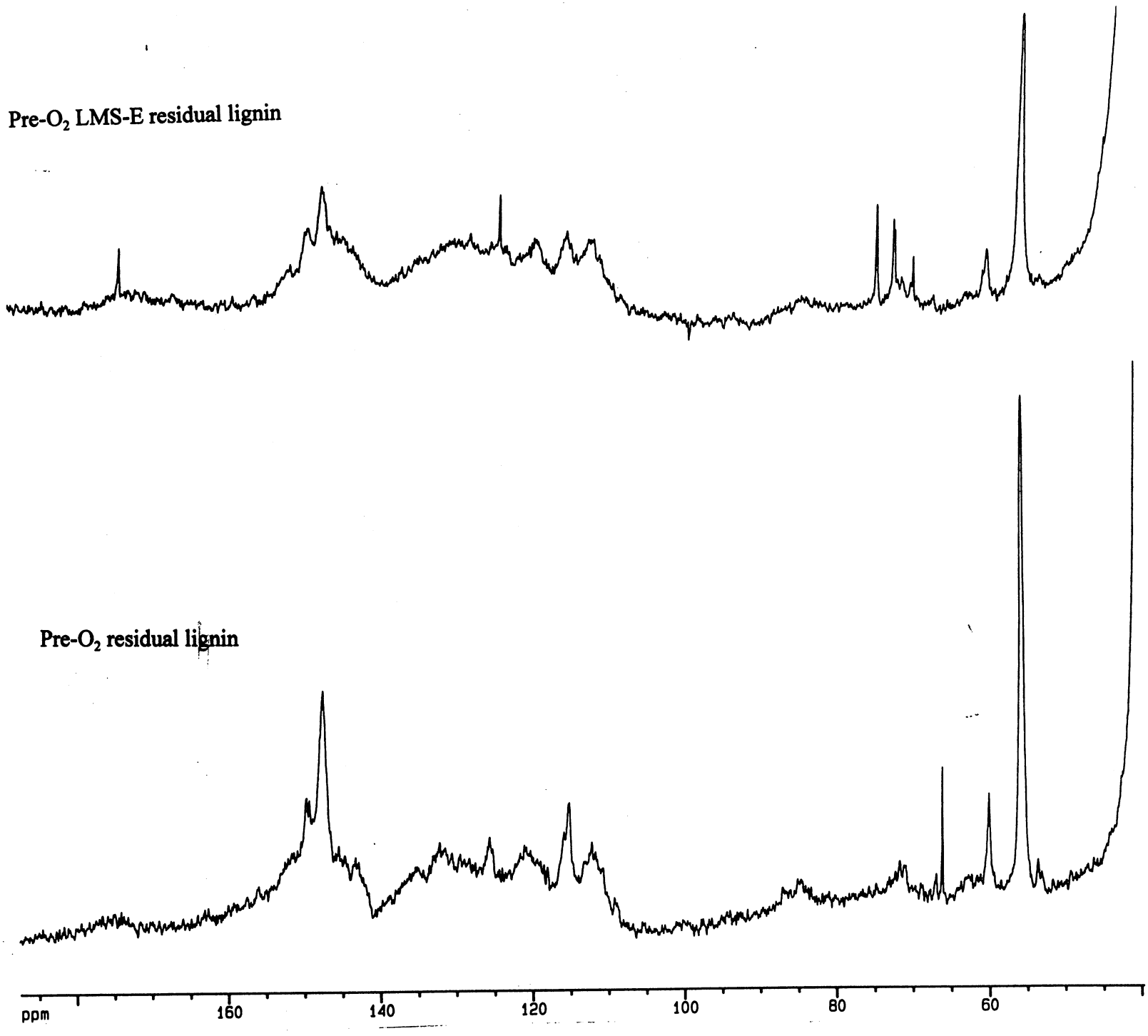
Pre-O_2 LMS-E residual lignin
Pre-O_2 residual lignin
ppm
160
140
120
100
80
60

Figure 3

Closed Mill Operation

PROJECT SUMMARY

PROJECT TITLE: Closed Mill Operation

PROJECT STAFF: Alan Rudie

FY 97 BUDGET: $50,000 (Sub-task Budget)

DIVISION: C&BSD

PROJECT NUMBER: F017

TASK OBJECTIVE: Evaluate metal binding to wood pulp.

TASK GOALS:

- Evaluate models for metal binding
- Evaluate competition for metal binding sites.

SUMMARY:

The selectivity coefficient relationship provides an accurate model of Calcium binding to wood pulp under controlled conditions. Competitive experiments with sodium and magnesium have been completed and offer an explanation for the release of calcium at high pH.

The X-ray spectroscopy effort has been expanded to include EXAFS spectrum of tightly bound iron. The EXAFS technique provides data on the first and second coordination sphere surrounding the metal. This result demonstrates that the iron environment is sufficiently uniform to obtain useful binding site information.

Because of the expense of continuing the X-ray spectroscopy effort, three research grant proposals have been filed to obtain funding. A proposal to the Georgia Consortium for Technological Competitiveness in Pulp and Paper has been recommended for funding and is awaiting approval of funds from the state legislature. A DOE Agenda 2020 proposal was rejected and an EPA proposal is under review. These proposals, if funded, will provide support for X-ray analysis of the binding sites of Manganese and Calcium as well as bulk and tightly bound iron. A student has entered the Ph.D. qualifiers with the intent of completing this X-ray effort.

FUTURE WORK:

If external funding is received, we will complete the X-ray EXAFS analysis of tightly bound iron

and one other metal. Competitive binding experiments will be completed for calcium, manganese, magnesium, sodium, barium and potassium. These should provide suitable models for predicting the metal binding behavior of wood pulps.

STATUS REPORT:

PROJECT TITLE: Closed Mill Operation PROJECT NUMBER:F017

TASK OBJECTIVE: Evaluate metal binding to wood pulp

INTRODUCTION:

Metals management in the paper industry has been around for a long time, principally related to control of transition metals in peroxide bleaching of high yield pulps.[1] The recent interest in alternative bleaching chemicals and in eliminating the bleach plant wastewater stream, has added a new dimension to the metals management problem. The potential for metals build-up in closed mills has created a need for a much better understanding of metal binding in wood pulp. The residual metals after acid or chelation treatment can potentially accumulate later in the bleach plant in mills using direct counter current washing with an acid bleach stage following extraction. Under the acid conditions, the remaining metal is released by the fiber to be re-adsorbed by the incoming pulp on the extraction washer. For example, a second/final ozone stage, cairo's acid, peracetic acid, mixed acids and dimethyldioxirane bleaching are all carried out under conditions where this is a problem. Improving the efficiency of metals removal in the first Q stage can reduce the second stage metals input to a level where it is not an issue. Improving our understanding of metal behavior can enable other cost effective engineering and operating solutions to the problems.

Acid leaching, and DTPA chelation have been evaluated under a variety of conditions. They successfully remove over 90% of the manganese, calcium and magnesium, but only about 50% of iron.[2] Much of the remaining metal is not technically bound to pulp, but is dissolved in the swollen fiber at approximately the same concentration as the surrounding water. Increasing the chelant dose, or treatment temperature, and extending the treatment time can improve metals removal efficiency to an extent but on manganese, DTPA doses above 0.2% on pulp, treatment temperatures greater than 75° C and treatment times beyond 30 minutes show little incremental gain.[3] Dilution or a second treatment will be more effective with most of the divalent metals. Iron behaves in a similar manner, but the residual level of iron, resistant to removal, is generally much higher. There is little likelihood that significant improvements in the performance of acid wash and aminocarboxylate treatments can be achieved and novel chelation approaches will be required if improved performance is to be achieved in this area.

Accurate models of metal binding are needed so that mills and engineering firms can estimate the accumulation of metal in various areas of the process and develop solutions that prevent scale formation and bleach chemical decomposition. Initial efforts to understand metal binding in pulp used solution equilibrium expressions to model the binding behavior. Although these methods can describe the sudden transformation from a bound state to dissolved state at a pH around 4, they do not predict the residual bound metal accurately at pH 3 and pH 5. Recently, there have been a number of more detailed approaches to explaining metal behavior. Towers and Scallan claim the behavior can be adequately predicted by the Donnan Equilibrium theory. Their results do appear to explain the differences in behavior of monovalent, divalent and trivalent metals, but cannot explain competition between metals effectively, and still has considerable error in the pH regions from 3.0 to 3.5 and around pH 5.[4] Laine, et al. claim the acid/base behavior of pulp shows

evidence of two different carboxylic acid functional groups, one a pKa 3.3-3.5 and the second with a pKa above 5.[5] They also invoked an electrical double layer/capacitance effect to completely explain their results. Ohlsson and Rydin contend that the use of selectivity coefficients adequately explains the behavior of metals in pulp, and demonstrate selectivity coefficients of about 9 between magnesium and sodium, and around 3 between calcium and magnesium.[6] Recently Fernandez Diniz evaluated several of these methods and concluded that the selectivity coefficient provided the most accurate model.[7] The Donnan approach cannot explain competition between metals of like charge and still appears to have significant error. The Laine approach is complex and has yet to provide a credible source for the second ion exchange site. Initial efforts in this project have focused on the selectivity coefficient approach.

Obtaining useful detailed on metals at natural concentration levels is quite difficult. In wood pulp made from normal wood sources, calcium starts near 1000ppm, manganese near 100 ppm and iron around 20 ppm. After conventional bleaching, acid treatment or chelation, calcium and manganese are almost completely removed, and iron ends up at 5 to 10 ppm. At these concentration level, most spectroscopic techniques are unable to provide useful information. Bailey and Reeve have reviewed several methods suitable for very low metal concentrations, and presented results from EDXA and secondary ion mass spectroscopy.[8] These methods indicate the iron and manganese are concentrated in the middle lamella and calcium is more uniformly distributed in the fiber wall. Although these methods have been useful for determining the spatial distribution of the metal, they have provided little useful information on how it is bound to the wood.

A spectroscopic technique that is useful at the 10 ppm level is x-ray fluorescence spectroscopy. In this technique, an electron is ejected from a core level orbital. When a valence electron falls down to fill the vacancy, the atom emits a characteristic X-ray. Several techniques are used but the methods of most interest are XANES, (X-ray Absorption Near-Edge Structure) which gives pertinent information on metal oxidation state and in some cases site symmetry, and EXAFS (Extended X-ray Absorption Fine Structure) which provides information on the first and second coordination sphere around the metal. The XANES technique sweeps the X-ray frequency through the edge or side of the absorption peak for the element of interest. Changes in the oxidation state of the atom result in changes in the energy of the core and valence level electrons, causing a shift in the leading edge of the X-ray absorption. The EXAFS technique concentrates on the variation in fluorescent intensity of the spectral region trailing the X-ray edge. These variations contain information similar to an X-ray powder pattern, but specific for the site surrounding the exited atom.

Synchrotrons have a number of advantages as X-ray sources. The X-ray emission is intense, already collimated and highly polarized. The collimated source allows the X-rays to be focused with mirrors set at a glancing angle, and the polarization of the X-rays reduces background scatter. Beam size is selected by placing a pin hole aperture in the beam. These features can be used to improve sensitivity and/or focus the X-rays into a microprobe that determines elemental abundance on a μ to mm scale. Using a monochromator to select an X-ray wavelength, the spectrometer can be set to sweep the wavelength through the X-ray absorption edge to obtain information on the oxidation state and local binding environment. Even with the X-ray intensity of the synchrotron at Brookhaven, obtaining useful information at the low concentrations in pulp samples was in doubt. Our success here offers a unique opportunity to get positive identification of specific binding

environment that will improve our understanding of the metal behavior.

SUMMARY OF PRIOR WORK

Alternative Metals Removal Methods:

A series of experiments were carried out, to determine the efficiency of alternate metals control methods relative to conventional chelation and acid treatments. In these experiments, pulp was treated with acid, DTPA, acetylacetone or potassium fluoride as metals control methods. The pH was varied from 1.5 to 7. The metals removal or residual metals content can then be plotted against pH to evaluate the efficiency of each reagent. In particular, acetylacetone and DTPA should function best at a pH above the pKa for the carboxylic acid groups in DTPA and the methylene protons in the metal complexed acetylacetone.

With manganese, calcium and magnesium, KF, Acid and acetylacetone all showed a step change in residual metal concentration between the pH 3 and pH 5 experiments. For example, manganese concentrations for the starting pulp and for the samples treated at pH 7 with H_2SO_4, acetylacetone and KF all fall in the range between 100 and 74 ppm. At pH 5, all fall in a range between 45 to 75 ppm. At pH 3, all fall in the between 0 and 10 ppm. Potassium fluoride and acid treatment were both evaluated at pH 1.5 where the residual manganese was below 1 ppm. There are two distinct differences with the results on iron. First, KF and sulfuric acid do not show the step change loss in iron but rather show a smooth, almost linear drop from about 15 ppm iron in the starting pulp to about 6 ppm iron at a pH of 1.5. Only acetylacetone shows the expected step change with the residual iron dropping from 14 to 15 ppm at pH 5 to about 6 ppm at pH 3. In these experiments, DTPA was evaluated at pH 7 and pH 5. It did not show the expected decrease in residual metal content.

These experiments demonstrated that the fluoride ion does not help hold the alkali earth metals in the pulp and does not contribute significantly to the metals removal process. Acetylacetone functions like a typical chelating agent but cannot reduce the iron content below the "hard to remove" threshold.

X-Ray Analysis of Iron

Previously, 4 samples had been analyzed using beam X26A at the National Synchrotron Light Source in Brookhaven. Working with us on this project are Dr. Paul Bertsch and Dr. Douglas Hunter of the University of Georgia Savannah River Ecology Laboratory.

One sample tested was a bleached sawdust pulp with an expected iron content around 35 ppm of hard to remove iron. The second sample was an unbleached softwood with an iron content of 13 ppm. The third was a mild acid treated sample with 10 ppm iron, the fourth was a DTPA treated sample of the same pulp with the iron content reduced to 11 ppm. The bleached sawdust sample was scanned using the 20 μ microprobe in white light mode (broad spectrum X-ray irradiation). It did not show any significant concentrations of iron, typical of contamination from rust or process metals. However, the metal was not distributed completely uniformly in the sample. All four

samples were evaluated using monochromatic irradiation scanning the iron X-ray absorption edge. Both the unbleached pulp and the mild acid treated pulp show predominately iron (III) character; the X-ray absorption edge was between the X-ray edge standards for Fe(II) and Fe(III), suggesting a mixture, but about 90% Fe(III). The sample treated with DTPA in which about 25% of the iron has been removed gives an X-ray Absorption edge suggesting about 40% iron (II) and 60% iron (III). The bleached sawdust pulp sample was similar to the DTPA sample, with the X-ray absorption edge indicating 20 to 30% Fe(II) content.

Summary of Recent Results

The EXAFS technique has been applied to two samples with low iron contents, an acetyacetonate complexed sample and an acid treated sample. Both spectra were obtained with extended runs of about two days each. These results demonstrate that the binding environment of tightly bound iron is sufficiently uniform to characterize and the Brookhaven instrumentation is capable of obtaining useful spectra. Our collaborators in this effort include Dr. Bertsch and Dr. Hunter at SREL and Dr. Ken Kemner with Argonne National Labs. This effort is currently on hold, waiting for the additional funding (*vide infra)* and a student to finish the qualifiers for the Ph.D. program.

The remainder of the effort has focused on competitive binding. Two approaches have been taken. A Masters candidate is using a sodium and a calcium electrode to monitor the changes in these metal concentrations when pulp is added, and as other metals are added. This work is on-going and will be reported at the next annual review when it is completed. The second approach has used elemental analysis with the ICP to determine the metals bound to pulp under controlled conditions. Pulps are fractionated in the Bauer McNett to remove fines, and acid washed twice at pH 1.5 and 70 ° C for 90 minutes. The pulp is then soaked in 0.01 M $CaCl_2$ and the pH adjusted to 7.0. The pulp in calcium form is washed thoroughly with nano-pure water and then leached over night in nano-pure water. It is then thickened to 20% consistency on a Buchner funnel, fluffed and placed in bags for storage.

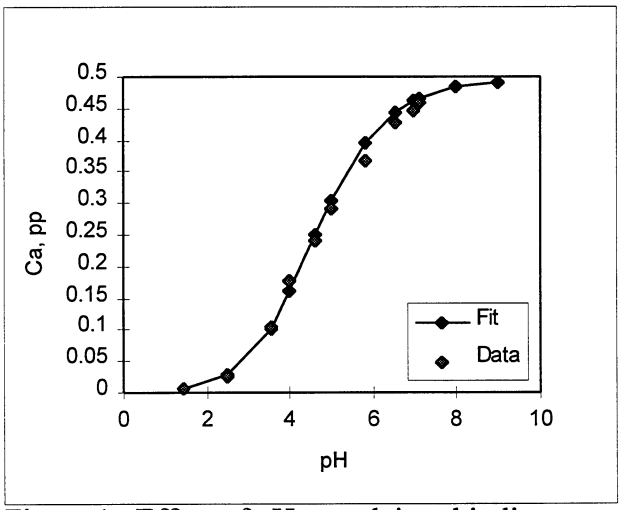

Figure 1. Effect of pH on calcium binding.

Experiments are carried out by diluting 10 OD grams of pulp to 1 liter with either nono-pure water, or a solution containing the competing metal. The pH is adjusted to target with either sulfuric acid or sodium hydroxide and the sample mixed for the specified time period using a U-shaped polypropylene stirrer. The sample is dewatered on a Buchner funnel and the pulp pad pressed to approximately 50% consistency using the TAPPI handsheet press set for 98 psi. Pressed pulps are weighed so the metals content can be adjusted for dissolved metals.

Pulps in the calcium form have been treated at various pH levels for either 30 or 120 minutes to

determine the effect of treatment time on the residual metals. A third experiment was carried out in 1 M NaCl to collapse the electrical double layer, and reduce the capacitance effect and fiber swelling effects on metal desorption. There is very little difference in the residual metal level between the 30 minute and 120 minute experiments and it has been concluded that 30 minutes is sufficient for most work.

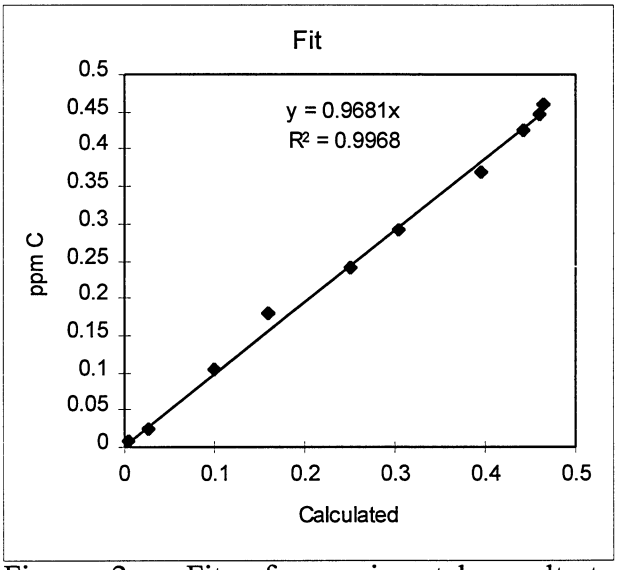

Figure 2. Fit of experimental result to calculated bound calcium.

The samples treated with 1 M NaCl all show less than 45 ppm remaining bound calcium. Instead of just helping to collapse the electrical double layer and minimize swelling effects, the sodium has also competed for the metal binding sites and displaced the calcium. Since the concentration of sodium exceeds the concentration of calcium by approximately 4,000 to 1, this outcome could have been anticipated. Analysis of this data using the selectivity coefficient approach has been successful at modeling the metal adsorption.

$2RH + Ca^{++} \Leftrightarrow 2R^{-} + 2H^{+} + Ca^{++} \Leftrightarrow CaR_2 + 2H^{+}$

$$K_H^{Ca} = \frac{(CaR_2)[H^+]^2}{[Ca^{++}](HR)^2}$$

or

$$Log(K_H^{Ca}) = aLog\frac{(CaR_2)}{[Ca^{++}]} + bLog\frac{[Na^+]}{(NaR)}$$

Where (CaR_2) and (NaR) are expressed as mole fraction of the available ion exchange sites, and Na^+ and Ca^{++} are in moles/liter. Bound calcium is adjusted for dissolved calcium by calculating the dissolved calcium concentration and subtracting the amount expected to be included with the water remaining in the sample. The log calcium ratio is plotted against the log proton ratio giving a straight line relationship with the intercept as log K and the slope as either a or b. For the calcium case, log K is 0.9355 and a = 1.606 with an $r^2 = 0.996$. The fitted curve parameters listed above gave a systematic error, with the experimental result giving slightly higher calcium contents than the fitted curve. A minor slope (exponent) adjustment from 1.6 to 1.45 improved the fit. This is the calculated curve shown in figure 1. Figure 2 shows the experimental data graphed against the fitted data. The regression line with an intercept of zero, slope of 0.968 and r^2 of 0.997 attest to the accuracy of the fitted result.

The exponent suggests a stoichiometry of approximately 3 calcium's for every 2 bound protons displaced. This is an unlikely explanation, and the result needs additional evaluation. The selectivity approach has, however, fit the data quite accurately and provides an empirical method to develop useful modeling results for eventual use in an equilibrium solver and mass balance calculations.

A second series of experiments was undertaken to begin evaluating metal competition and confirm the earlier sodium results. These experiments were carried out as before, but the solution was made up to a molar strength of either NaCl or $MgSO_4$. The sodium replaces calcium at concentrations of 0.1 and 0.01 M, but has little observable effect at 0.001 M. Sodium to calcium ratios are approximately 400 to 1, 40 to 1 and 4 to 1 respectively. Magnesium competed strongly with the calcium and resulted in reduces calcium levels at all three concentrations, 0.01, 0.005 and 0.001 M. The approximate molar ratios in this case are 40 to 1, 20 to 1 and 4 to 1. The magnesium results are shown in figure 4.

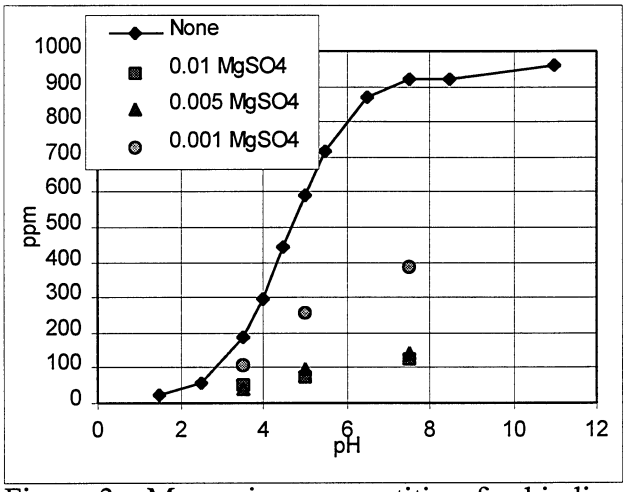

Figure 3. Magnesium competition for binding sites.

Fitting this data to a selectivity coefficient relationship requires a simultaneous fit to pH. Since this is considerably more complex than the straight pH relationship reported above, it has not been completed, but it is expected that this type of approach will work. Initial efforts with the sodium data does give the expected squared relationship to sodium at high pH, but it is not clear that this will also fit at the lower pH.

REMAINING WORK

Planned experimental work is to complete the competitive metal modeling effort. Initial experimental work will focus on models for calcium and sodium. Once a reliable approach has been established, the effort will expand to evaluate the competition between calcium, magnesium, sodium and manganese.

Three grant applications have been filed for continuing the X-ray work and supporting other aspects of this project. A Georgia Consortium grant ($115,000) has been recommended for funding and is waiting approval of the legislature of the Georgia Consortium funding request. A DOE 2020 proposal ($1,499,400) was turned down, and an EPA/NSF proposal ($269,000) is still waiting completion of the review. The Georgia Consortium proposal is primarily XANES and EXAFS, working with staff at the Savannah River Ecology Laboratory and faculty at Georgia Tech. The EPA proposal will also support the equilibrium and modeling efforts.

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Sulfur-Free Selective Pulping Process

PROJECT SUMMARY

PROJECT TITLE:	SULFUR-FREE SELECTIVE PULPING PROCESS
PROJECT NUMBER:	3661
PAC:	Chemical Pulping and Bleaching
DIVISION:	Chemical and Biological Sciences
PROJECT STAFF:	Donald Dimmel, Elizabeth Althen
BUDGET (FY 96-97):	DOE - $230,500; IPST - $0
SUPPORTING RESEARCH:	Three M.S. Students
RESEARCH AREA:	Improved Pulping Processes

OBJECTIVE:

The objective of this project is to develop improved pulping processes by synthesizing and utilizing low-cost catalysts that will increase pulping rates and product yields, while reducing the dependence on sulfur additives. The goal is to prepare useful quinone-type catalysts that have a cost equivalent to ~$1.00/lb. anthraquinone (AQ). Most of our research has centered on preparing 2,6/7-dimethylanthraquinone (DMAQ) from lignin, an inexpensive pulping by-product.

SUMMARY OF RESULTS:

A joint research effort between IPST and the National Renewable Energy Laboratory (NREL) is being conducted on ways to produce cost-effective pulping catalysts. The catalysts-from-lignin process involves treating a lignin with an oxidizing agent to give 2,6-dimethoxybenzoquinone (DMBQ), which is then treated with isoprene to give a mixture of compounds, the principal component of which is dimethylanthraquinone (DMAQ). The cost of the catalyst-from-lignin is highly dependent on the yield of the synthesis steps and the cost of the oxidant in first step.

Previous work has concentrated on the oxidation of hardwood lignins (and models) by nitrogen dioxide (NO_2) in methanol to give DMBQ. We have now perfected an alternate way (that is a variation of the NO_2 chemistry) for conducting the oxidation. The DMBQ yields are slightly improved, with significantly lower chemical requirements; consequently, the step can be done much more cheaply than the standard NO_2 treatment. The cost of preparing a catalysts mixture containing DMAQ from lignin now appears to be below $3.00/lb. The uncertainty is because we have recently found (1) an improved method for conducting the oxidation step, but (2) have had recent difficulty matching our early good yields in the second synthetic step.

We have also developed an alternative procedure for preparing DMAQ. Benzoquinone is treated with isoprene at high temperatures to give a high yield of a mixture of bis-adducts. These bis-adducts, which are non aromatic versions of DMAQ, can

be quantitatively oxidized by base and oxygen to DMAQ. The cost of DMAQ by this procedure depends strongly on the cost benzoquinone; assuming a 90% conversion of phenol or benzene to benzoquinone by reported patents, the cost has been estimated by Arthur Power, a technoeconomic consult at NREL, to be ~$1.70/lb.

Pulping studies have confirmed that DMAQ is twice as effective as AQ in soda/AQ, kraft/AQ and polysulfide/AQ pulping, and that the bis-adduct is only slightly less active than DMAQ. [The latter result suggests that much of the bis-adduct is converted to DMAQ during pulping.] The cost effectiveness of DMAQ by either synthetic route looks very promising; we are close to our goal of an equivalent $1/lb AQ catalyst.

Future research will focus on larger scale pulping experiments with pure DMAQ, mixtures from isoprene-DMBQ reactions that contain DMAQ, and the bis-adducts from an isoprene-benzoquinone reaction. Our aim is to produce enough pulp to evaluate strength properties and bleachability characteristics. We will be assessing catalyst performance under a variety of pulping conditions, including extended delignification. Continue efforts will be directed to improve the yields/cost of the lignin oxidation and isoprene-DMBQ step. Further assessments of ways to isolate DMBQ from lignin reactions is needed if this route is to be successful.

In summary, we have developed two attractive ways to make an inexpensive, potent pulping catalyst, DMAQ. The one path from lignin has the advantage of a cheap starting material, but the process is somewhat complex relative to isolation of materials, etc. The other path is a high yield one step synthesis from a chemical of unknown cost. Addition efforts are needed to accurately define catalyst costs and pulp properties for cooks done with the new catalyst.

TECHNICAL PROGRAM REVIEW

DATE: March 10, 1997

PROJECT TITLE: SULFUR-FREE SELECTIVE PULPING PROCESS

PROJECT STAFF: Donald Dimmel, Elizabeth Althen

BUDGET (FY 96-97): DOE - $230,500; IPST - $0

DIVISION: Chemical and Biological Sciences

PROJECT NUMBER: 3661

OBJECTIVE:

The objective of this project is to develop improved pulping processes by synthesizing and utilizing low-cost catalyst that will increase pulping rates and product yields, while reducing the dependence on sulfur additives.

GOALS:

1. The prime goal of this research is to prepare useful quinone-type pulping catalysts that have a cost equivalent to ~$1.00/lb. anthraquinone (AQ). Most of our research has centered on preparing 2,6/7-dimethylanthraquinone (DMAQ) from lignin, an inexpensive pulping by-product. However, alternative preparations of DMAQ from non lignin sources is also within the scope of this project.
2. In order to accomplish the prime goal, we must demonstrate that a quinone mixture, containing DMAQ and related structures, is an effective pulping catalyst.
3. In order to accomplish the prime goal, we must demonstrate that pulping with DMAQ does not have detrimental affects on paper strength properties.
4. In order to accomplish the prime goal, we must develop a simple, inexpensive synthetic procedure for DMAQ that can be practiced commercially.

SUMMARY:

A joint research effort between IPST and the National Renewable Energy Laboratory (NREL), with funding from the Department of Energy, is being conducted on ways to produce cost-effective pulping catalysts. The catalysts-from-lignin process involves treating a lignin with an oxidizing agent to give a mixture of benzoquinones, which are then converted into non-aromatic dimethylanthraquinone (DMAQ) precursors by treatment with isoprene (Diels-Alder reaction); final conversion of these precursors to DMAQ occurs by loss of methanol and hydrogen, either during reaction or in a separate step (Figure 1).

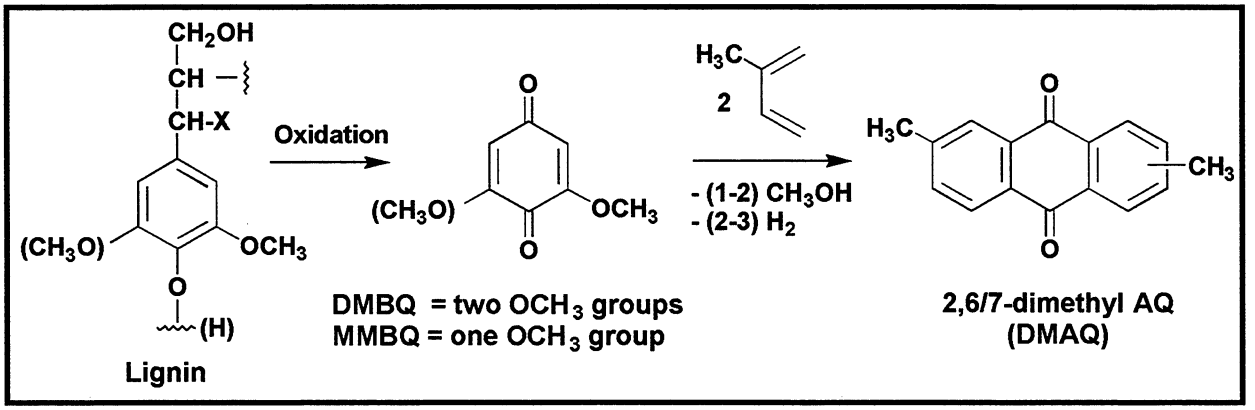


Figure 1. Chemical steps in the conversion of lignin to DMAQ.

The cost of preparing a catalysts mixture containing DMAQ from lignin appears to be below $3.00/lb. The uncertainty is because we have recently found (1) an improved method for conducting the oxidation step, but (2) have had recent difficulty matching our early good yields in the aqueous Diels-Alder step.

An alternative procedure that we have recently examined is outlined in Figure 2. Benzoquinone (BQ) is treated with isoprene at high temperatures to give nearly a quantitative yield (by GC analysis) of a mixture of bis-adducts. The latter can be quantitatively oxidized by base and oxygen to DMAQ. The cost of DMAQ by this procedure depends strongly on the cost BQ; assuming a 90% conversion of phenol or benzene to BQ by reported patents, the cost has been estimated by Arthur Power, a technoeconomic consult at NREL, to be ~$1.70/lb.

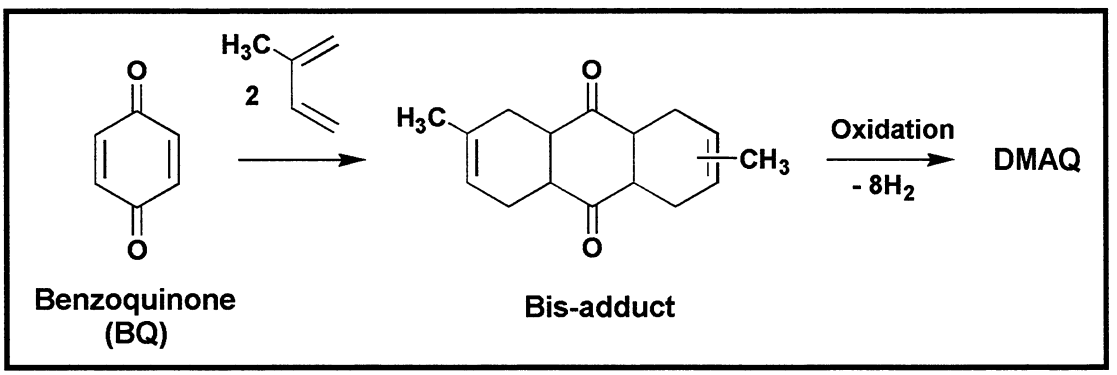


Figure 2. Chemical steps in the conversion of BQ to DMAQ.

Additional pulping studies have confirmed that DMAQ is twice as active as AQ and that the bis-adduct is only slightly less active than DMAQ. [The latter result suggests that much of the bis-adduct is converted to DMAQ during pulping.] The cost effectiveness of DMAQ by either synthetic route looks very promising; we are close to our goal of an equivalent $1/lb AQ catalyst.

INTRODUCTION

The research reported here outlines work done at IPST since the last Status Report. A description of the joint research with NREL is available in our annual reports to DOE. The research at NREL compliments IPST research by examining alternative chemical synthesis methods, providing ways to get suitable lignin starting materials, and conducting technoeconomic evaluations. The focus of our recent research has been (1) continued studies to improve the overall yield of DMAQ from lignin, (2) to develop a new, possibly more cost effective, synthesis of DMAQ for a non lignin starting material, and (3) to demonstrate the pulping activity of DMAQ and the bis-adduct precursor of DMAQ in polysulfide and soda systems, respectively.

RECENT RESEARCH RESULTS

DMAQ-from-Lignin: the Oxidation Step

The cost of the catalyst-from-lignin is highly dependent on the yield of the synthesis steps and the cost of the oxidant in first step. Previous work has concentrated on the oxidation of hardwood lignins (and models) by NO_2 in methanol to give DMBQ. We have now perfected an alternate way (that is a variation of the NO_2 chemistry) for conducting the oxidation. The DMBQ yields are slightly improved, with significantly lower chemical requirements; consequently, the step can be done much more cheaply than the standard NO_2 treatment. Needless-to-say, there have been many optimization studies performed; however, until certain patent issues are resolved, we can not discuss the procedure involved.

There are issues that need to be resolved concerning the isolation of DMBQ from oxidized lignin reaction mixtures. In model oxidations, the DMBQ readily precipitates from the methanol solvent and is easily isolated. However, in lignin oxidations, the DMBQ shows a solubility in the methanol in excess of known solubility. We suspect that there is an attraction between the DMBQ and the dissolved lignin. Roughly 80% of the Repap lignin dissolves in methanol. [The insoluble portion provides no DMBQ upon oxidation.] An inexpensive separation of DMBQ from the reaction mixture needs to be found. At present, only a few options have been investigated.

With regards to older NO_2 studies, we have examined Kenaf as a starting material. Kenaf lignin is known to have a high ratio of syringyl to guaiacyl units and, therefore, might be expected to be a good starting material for the synthesis of pulping catalysts from lignin. Kenaf core and bast were pulped separately with NaOH. The resulting lignins were isolated and treated with NO_2 in anhydrous methanol to give DMBQ in 1.3% and 3.5% yield, respectively. This surprising result indicates that Kenaf is not an appropriate starting material.

Regardless of the oxidation procedure employed, the yield of DMBQ will rise as the lignin molecular weight decreases. [There will be more of the reactive phenolic end units.] Therefore, we revisited the possible use of a copper oxide (CuO) lignin pretreatment. Previous work has shown that treatment (170°C, 1-5 hr) of lignin with an excess (7.5 equiv.) of CuO in aqueous NaOH resulted in significant depolymerization of lignin. The principal monomeric products formed by this pretreatment step were identified as vanillin, acetovanillone, vanillic acid, syringaldehyde, acetosyringone and syringic acid. The yield of DMBQ, obtained from NO_2 oxidation of the CuO-treated lignin, was as high as 16.4%. This amounts to a two- to three-fold increase in the yield of DMBQ, as compared to the unfractionated lignin. However, the use of stoichiometric amounts of CuO or $Cu(OH)_2$ on an industrial scale is probably not practical.

Investigations into the possible use of catalytic quantities of copper for lignin depolymerization were undertaken since it is well known that Cu (I) is readily oxidized to Cu (II) in the presence of oxygen. We have observed poorer DMBQ yields from the NO_2 oxidation of CuO/O_2-treated lignin than an untreated lignin (5.1%); however, the yield was better when 0.50 equivalents of CuO were used than for 7.5 equivalents (4.1 vs 2.9%). Most likely, the oxygen caused the aldehyde, CuO products to be further oxidized to NO_2-inactive acidic products. Consequently, this method does not appear to be very promising.

DMAQ-from-Lignin: Diels-Alder Step

The Diels-Alder reaction between DMBQ and isoprene gives a mixture of mono- and bis-adducts (two and three ring structures), along with the desired DMAQ (Figure 1). Some of the bis-adducts are converted to dimethylanthraquinone (DMAQ) upon isolation by chromatography; these components will likely do the same transformation during pulping and, thus, contribute to the mixture's pulping activity. The other components will be inactive. The formation of DMAQ in the aqueous Diels-Alder reaction is a consequence of losing two methanol and hydrogen units. The lost of the hydrogen is considered to be a result of a set of disproportionation reactions, in which hydrogen is being transferred from one bis-adduct to another, the one becoming richer in double bond units and the other becoming poorer.

It is now becoming obvious that there are subtleties associated with the aqueous Diels-Alder reaction that we do not understand. When we first discovered this chemistry, the yield of mono- and bis-adducts were 18 and 65%, respectively. The good yields of bis-adducts likely can be traced to the production of a fully aromatic naphthaquinone mono-adduct. A combination of loss of one methanol group and disproportionation of non aromatic mono-adducts leads to 2-methoxy-6-methyl-naphthaquinone. The latter will be much more reactive than a non aromatic mono-adduct towards a second isoprene addition. Good yields of DMAQ hinge on promotion of rapid disproportionation reactions instead of enolization to an inactive naphthahydroquinone (Figure 2).

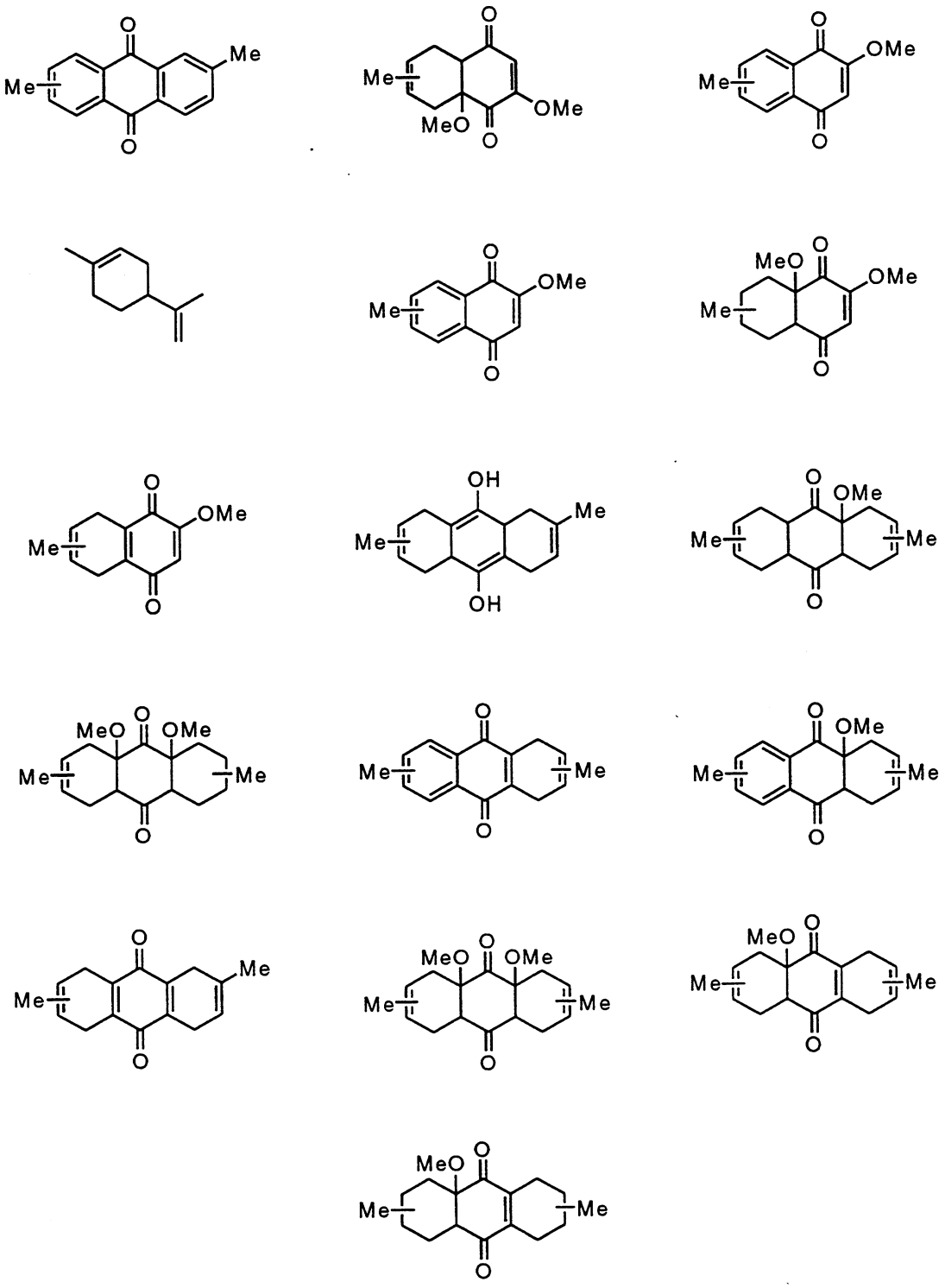


Figure 1. Components in the Aqueous DMBQ/Isoprene Diels-Alder Reaction.

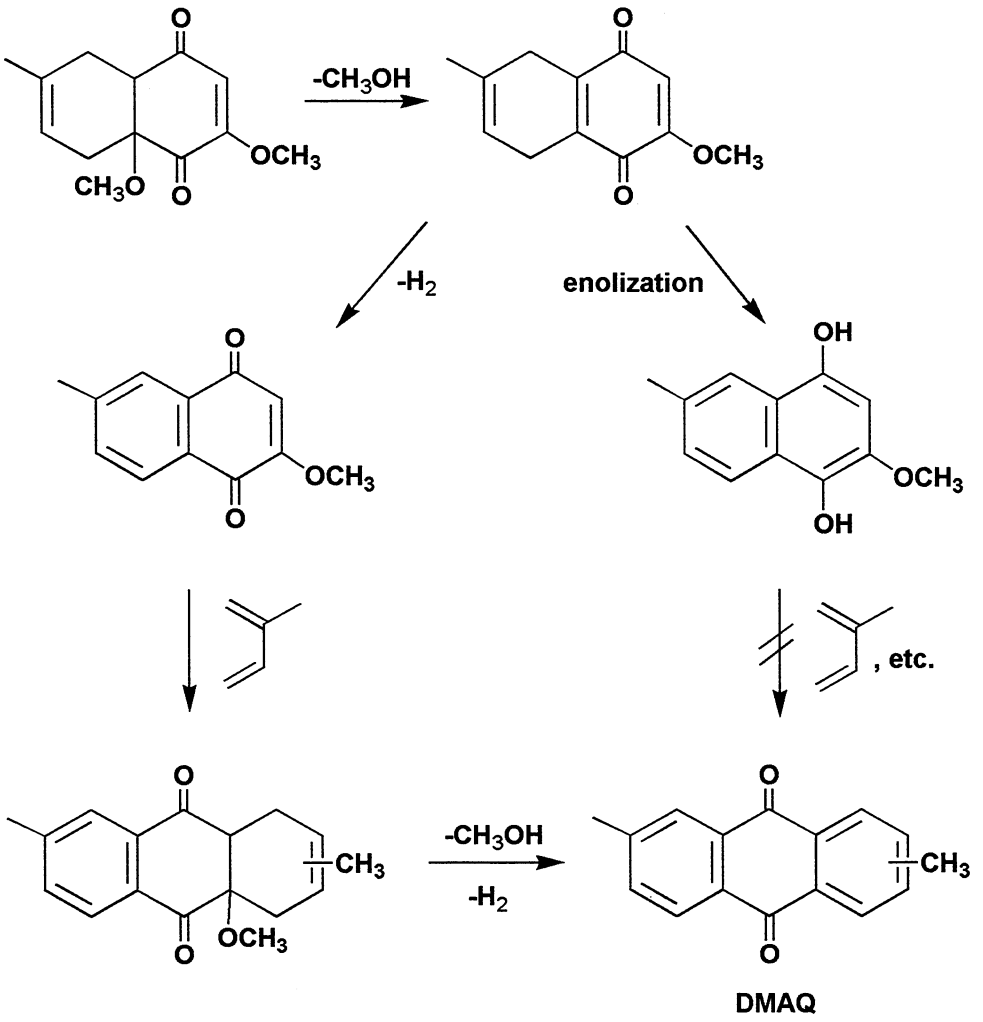


Figure 2. Proposed Reactions of a Mono-Adduct to give DMAQ.

Recent reactions have provided poor yields (~5%) of DMAQ and bis-adducts in general. A couple of years ago the DMAQ direct yield was 30% and after chromatography was 40%. So, what has changed? We are using a new batch of DMBQ starting material and nanopure water. Maybe the pH of the solution is different (high or low pH will promote enolization reactions. Maybe there are differences in the content of trace metals in the water or prepared DMBQ that adversely effect the rate of disproportionation. At this point, we are examining several of these possibilities.

The value of water as a solvent in Diels-Alder reactions has been attributed to a rate enhancement due to entropy effects, "micellular catalysis;" there is a reduction in the difference between the volume associated with the product and that of the hydrophobic reactants. Since changes in solvent can often have dramatic effects on the course of Diels-Alder reactions, we decided to examine solvent effects on the isoprene-DMBQ reaction to make certain that water was the best Diels-Alder solvent. The results, as

shown in Table 1, verified that water was the best of the solvents examined. Note that the DMAQ yield in water for this study, which was completed before our new DMBQ arrived from NREL, was still not as good as previously observed.

Table 1. Diels-Alder Reactions of DMBQ and Isoprene in Various Solvents[a]

Solvent	Isoprene:DMBQ (molar ratio)	Percent				
		DMBQ	MMNQ	Mono-adduct	Bis-adduct	DMAQ
Neat	3:1	31	2	none	none	0.5
Hexane	3:1	16	8	none	none	none
Ethyl ether	3:1	20	9	none	none	none
Ethyl acetate	3:1	15	11	none	none	none
Acetone	3:1	24	9	none	none	none
Isopropanol	3:1	4	17	10	0.9	0.4
Butanol	3:1	none	9	11	2	none
Acetic Acid	3:1	5	8	6	12	none
Methanol	3:1	17	28	none	none	14
Methanol	6:1	3	28	8	3	18
Methanol	10:1	1	29	16	7	8
Water	3:1	none	4	none	11	22
Water	6:1	none	2	9	20	17
Water	10:1	none	none	none	18	21

[a] Reactions were carried out in steel bombs (4.0 mL capacity) at 160 °C for 16-17 h.

As the polarity of the reaction mixture decreased, the quantity of bis-adducts and DMAQ present in the product mixture also decreased; some DMBQ was recovered in the non-aqueous cases. Also, in many cases, the major product was 2-methoxy-6-methyl-naphthaquinone (MMNQ). This component may, in part, be formed during the GC analysis through loss of methanol and oxidation of a mono-adduct. The modest yields of these products from reactions carried out in methanol and water suggests that increasing the molar ratio of isoprene to DMBQ should result in an increase in the amount of DMAQ formed; however, this was not observed.

Since, as mentioned earlier, DMBQ is difficult to separate from lignin, we tested the practicality of performing the Diels-Alder reaction on the crude lignin-DMBQ mixture. Treatment of the mixture with isoprene (5.5 or 27.5 equivalent) resulted in very low yield (0.4 -4.3%) of DMAQ.

Bis-Adduct of Benzoquinone and Isoprene

Very early in this research project, we examined the Diels-Alder reactions of several substrates as means to understand differences between DMBQ and other dienophiles. One of the reactions examined was that of benzoquinone (BQ) with isoprene. We observed a 98% yield of two types of adducts: a mono-adduct in 30% yield and bis-adducts (mixture of isomers) in 68% yield. We have re-examined the reaction with

different solvents, reactant ratios, temperatures, and time and have found conditions that provide bis-adducts in high yields. Gas chromatography indicated a quantitative yield; the isolated (not optimized) yield from large scale runs have varied from 65-80%. The structure of the bis-adducts is shown in Figure 3. Treatment of the bis-adducts with oxygen and KOH in an organic solvent gave DMAQ in 93% isolated yield.

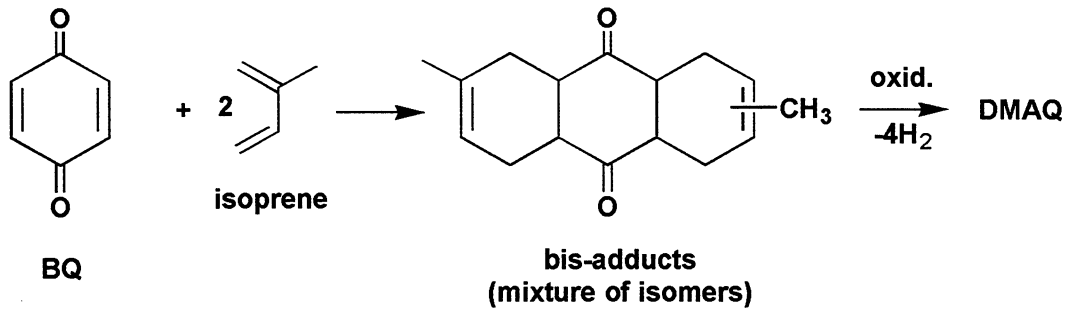


Figure 3. Preparation of DMAQ from Benzoquinone.

The potential advantages of this route to DMAQ are that it gives a "clean" product, the overall yield is very high, and less isoprene is used in comparison to the catalyst-from-lignin route. The major disadvantages may be the cost of the benzoquinone. The cost of DMAQ by this procedure depends strongly on the cost BQ; *assuming* a 90% conversion of phenol or benzene to BQ by reported patents, the cost has been estimated by Arthur Power, a technoeconomic consult at NREL, to be ~$1.70/lb. Since DMAQ is twice as active as AQ, this price is equal to $0.85lb. AQ. An accurate cost of benzoquinone, prepared on large scale, is needed.

Pulping Studies

A comparison has been made for the kappa numbers resulting from the soda/catalyst pulping of pine for pure 2,6/2,7-DMAQ and the mixture of bis-adducts made from BQ (Table 2). It appears that the bis-adduct mixture is slightly less active that DMAQ. Whether this deficiency is worth the cost of an extra synthesis step that it takes to convert the bis-adducts to DMAQ has yet to be determined.

Another set of cooks were performed to compare the pulping activity of DMAQ to AQ in conjunction with polysulfide on pine. A previous one-time, quick study suggested that DMAQ might be four times more active than AQ with polysulfide; however, the data had a fair amount of scatter. The new data, presented in Table 3, conclusively shows that the activity difference is a factor of two, not four. This factor of two also exists in soda and kraft pulping systems (earlier project results). Yield data on this and the bis-adducts pulping runs were not determined because the information can not be obtained with much accuracy in small scale experiments.

Table 2. Kappa Number Comparison of Soda/Catalyst Pulping of Pine.

Sample #	% Additive	K	Ave K	Std Dev	Ave K	Std Dev
1	0.05% 2,6/2,7-DMAQ	30.2	30.1	0.1	29.6	0.5
1	0.05% 2,6/2,7-DMAQ	30.0				
2	0.05% 2,6/2,7-DMAQ	30.2	29.8	0.7		
2	0.05% 2,6/2,7-DMAQ	29.3				
3	0.05% 2,6/2,7-DMAQ	29.0	29.1	0.0		
3	0.05% 2,6/2,7-DMAQ	29.1				
4	0.05% Bis-Adduct	32.4	32.1	0.4	30.6	1.3
4	0.05% Bis-Adduct	31.8				
5	0.05% Bis-Adduct	29.4	29.5	0.2		
5	0.05% Bis-Adduct	29.7				
6	0.05% Bis-Adduct	30.2	30.2	0.0		
6	0.05% Bis-Adduct	30.2				
7	0.10% Bis-Adduct	27.2	27.0	0.2	27.4	0.5
7	0.10% Bis-Adduct	26.8				
8	0.10% Bis-Adduct	27.9	27.7	0.3		
8	0.10% Bis-Adduct	27.6				
9	0.025% 2,6/2,7-DMAQ	30.3	30.0	0.5	31.7	1.5
9	0.025% 2,6/2,7-DMAQ	29.7				
10	0.025% 2,6/2,7-DMAQ	32.4	32.8	0.6		
10	0.025% 2,6/2,7-DMAQ	33.2				
11	0.025% 2,6/2,7-DMAQ	32.9	32.2	0.9		
11	0.025% 2,6/2,7-DMAQ	31.6				
12	0.025 % Bis-Adduct	34.5	34.9	0.5	34.5	0.5
12	0.025 % Bis-Adduct	35.2				
13	0.025 % Bis-Adduct	33.5	34.2	1.0		
13	0.025 % Bis-Adduct	34.9				
14	0.05 % Bis-Adduct	31.8	32.4	0.9	30.3	3.0
14	0.05 % Bis-Adduct	33.1				
15	0.05 % Bis-Adduct	28.3	28.2	0.2		
15	0.05 % Bis-Adduct	28.0				

Kappas for samples # 1-8 (cooked 1-31-97) were performed on o.d. pulp, whereas samples # 9-15 (cooked 11-26-96) were never dried pulp.

Table 3. Table 2. Kappa Number Comparison of Polysulfide/Catalyst Pulping of Pine.

Sample #	% Additive	Kappa #	Average K	Std. Dev.	4 Bomb Ave.	Std. Dev.
1	0.025% DMAQ	29.0, 29.0	29.0	0.0	29.4	0.8
2	0.025% DMAQ	28.6, 28.6	28.6	0.0		
3	0.025% DMAQ	30.0, 29.4	29.7	0.3		
4	0.025% DMAQ	31.2, 29.8	30.5	0.7		
5	0.05% AQ	33.1, 33.7	33.4	0.3	30.0	2.4
6	0.05% AQ	29.9, 29.0	29.4	0.5		
7	0.05% AQ	29.2, 29.7	29.4	0.3		
8	0.05% AQ	27.5, 28.0	27.8	0.3		
9	0.025% DMAQ	27.0, 26.8	26.9	0.1	26.8	1.0
10	0.025% DMAQ	25.2, 25.6	25.4	0.2		
11	0.025% DMAQ	28.0, 27.3	27.6	0.4		
12	0.025% DMAQ	27.6, 27.3	27.5	0.2		
13	0.10% AQ	25.5, 25.7	25.6	0.1	24.8	0.8
14	0.10% AQ	24.7, 25.8	25.2	0.6		
15	0.10% AQ	24.9, 24.3	24.6	0.3		
16	0.10% AQ	23.9, 23.7	23.8	0.1		

Cook Set #1, Samples # 1-8, 60 min from 100°C to 171/172°C, 70 min at 171/172°C
Cook Set #2, Samples # 9-16, 60 min from 100°C to 173/174°C, 70 min at 173/174°C

The difference in the final holding temperature between the two cooks is due to a malfunction of the controller for the oil bath in which the runs were performed.

It should be noted that many lessons were learned in these pulping experiments; the data presented represents is only the "tip of the iceberg" relative to the number of experiments performed. With small bomb cooks, chip variability is a big issue when attempting to get reproducible numbers. We hand crafted some thin chips and compared results to regular screened chips. We tried different methods of post-run screening, of kappa determinations on wet versus dry pulp, and of polysulfide determination. We encountered controller malfunctions, leaking bombs, and poor chip source (for several cooks). In the end, we were able to optimize the experiments with respect to chip size and pre- and post-run screening and obtained reproducible data sets. Standard operating procedures were developed that will greatly assist others who need to do similar studies.

SUMMARY

We have developed two attractive ways to make an inexpensive, potent pulping catalyst, DMAQ. The one path from lignin has the advantage of a cheap starting material, but the process is somewhat complex relative to isolation of materials, etc. The other path is a high yield one step synthesis from a chemical of unknown cost. Our results indicate that DMAQ is twice as effective as AQ in soda/AQ, kraft/AQ and polysulfide/AQ pulping.

FUTURE STUDIES

Future research will focus on larger scale pulping experiments with DMAQ and the bis-adduct mixture to produce enough pulp to evaluate strength properties and bleachability characteristics. We will be assessing catalyst performance under a variety of pulping conditions, including extended delignification. Continue efforts will be directed to improve the yields/cost of (1) benzoquinone from the lignin oxidation step and (2) the Diels-Alder step that follows. Further assessments of ways to isolate DMBQ from lignin reactions is needed if this route is to be successful.

Improved Selectivity in Ozone Bleaching

PROJECT SUMMARY

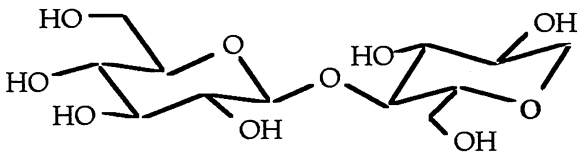
PROJECT TITLE:	IMPROVED SELECTIVITY IN OZONE BLEACHING
PROJECT NUMBER:	4168
PAC:	Chemical Pulping and Bleaching
DIVISION:	Chemical and Biological Sciences
PROJECT STAFF:	Donald Dimmel, Cathy Welder
BUDGET (FY 96-97):	USDA - $42,000
SUPPORTING RESEARCH:	Project F015
RESEARCH AREA:	Improved Beaching Processes

OBJECTIVE:

Our research is aimed at determining the fundamental mechanisms underlying ozone bleaching selectivity, with the ultimate goal being to improve ozone-pulp strength properties, to more fully integrate ozone into ECF (elemental chlorine-free) bleaching sequences and to facilitate mill closure. Ozone is a particularly attractive bleaching agent, since it removes large amounts of residual lignin with only a low application. However, the use of ozone is hampered by pulp quality issues; there appears to be too much cellulose damage. The research is directed at determining the extent to which cellulose is attacked by ozone directly and by reactive lignin and carbohydrate intermediates produced by ozone. Clarification of the relative importance of the reaction pathways will allow us to develop strategies to improve ozone selectivity.

SUMMARY OF RESULTS:

The fundamental study of cellulose oxidation and depolymerization reactions planned in this research will employ amorphous cellulose and 1,5-dianhydrocellobiitol (**1**), a cellulose model, as substrates. The model system allows us to follow various degradation reactions (cleavage pathways, functional group introduction) and develop an in-depth understanding of molecular changes. The methods developed will then be applied to the more complex amorphous cellulose case. At present, the methods being examined are NMR and GC of direct and derivatized product mixtures, respectively. Early experiments indicate that model **1** is fairly unreactive towards excess ozone. No structural changes are seen by NMR.



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Samples of amorphous cellulose have been prepared and preliminary ozonations conducted. A significant amount of cellulose dissolved due to the action of ozone. We are attempting to derivatize and analyze the molecular weight changes caused by the ozone reaction. Problems have been experienced with regards to the derivatization reaction and viscosity measurements on the amorphous cellulose. We believe that the selectivity of ozone reactions can be effectively monitored by examining molecular weight changes in amorphous cellulose in the presence of lignin (or lignin model compounds). Initial experiments are being done in the absence of the lignin component.

In summary, we are in the early developmental stages of the project - preparing materials and defining analytical procedures.

Technical Program Review

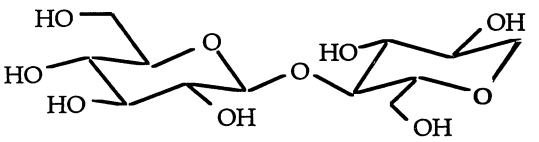
Project Title	Improved Selectivity in Ozone Bleaching
Project Staff	Donald R. Dimmel, Catherine O. Welder
Division	Chemical and Biological Sciences
Project Number	4168

Objective

The goal of this project is to better understand the detailed chemistry of pulp bleaching. Towards this end, we are leveraging our activities with financial support from the New Research Initiative program at the USDA. The USDA research activities compliment on-going work and allow us to expand our activities into other bleaching areas. The tools and techniques being developed in the USDA-sponsored research will be valuable for oxygen bleaching fundamentals (for example).

Summary

Our intent is to study reactions of both 1,5-dianhydrocellobiitol (**1**) and cellulose with ozone. 1,5-Dianhydrocellobiitol was chosen as a cellulose model because it is resistant to peeling reactions and has a β-(1-4) linkage similar to the linkages found in cellulose. We are interested in determining the location of carbonyl and carboxylic acid introduction in a cellulose model by nuclear magnetic resonance (NMR) spectroscopy combined with gas chromatography (GC), Fourier transform infrared (FTIR) spectroscopy, and deuterium labeling by sodium borodeuteride reduction of reaction products. For reactions of amorphous cellulose, we will monitor molecular weight changes by gel permeation chromatography (GPC). GPC will allow us to determine whether cellulose is degraded by step-wise peeling reactions or by random chain cleavages. We have developed a method for obtaining amorphous cellulose. We are in the process of fine-tuning the ozone generator reaction design. We are also currently developing methods (NMR, GC, and GPC) to analyze ozonation products.



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Introduction

Ozone has long been viewed as a potential alternative or supplement to chlorine-based bleaching reagents. In response to environmental pressures in 1970s, the paper industry built several ozone pilot plants to examine the feasibility of replacing chlorine with O_3. However, severe technical limitations at the time included the high expense of O_3, the difficulty in engineering a reactor that bleached uniformly with the highly reactive O_3, and the poor quality of the pulp produced. Today, many of these issues have been somewhat overcome and there are now fourteen worldwide installations of ozone facilities producing from 400 to 1600 tons of pulp per day; eleven are kraft mills.[1]

Despite the recent growth in the use of ozone in the pulp and paper industry, there is still a widespread reluctance to fully implement the technology, either in a TCF sequence, or as a supplement to a chlorine dioxide stage. One major reason is the extensive depolymerization of cellulose and accompanying pulp strength losses.[2,3] There are several potential pathways of cellulose depolymerization that could cause the poor selectivity of O_3 bleaching; however, the relative importance of each of these pathways remains unclear. A good understanding of the different mechanisms of cellulose depolymerization and the dependence of these reactions on reaction conditions should positively impact selectivity. As a result, ozone bleaching may routinely produce high quality pulps and the full environmental benefits of an oxygen-based bleaching reagent may be realized.

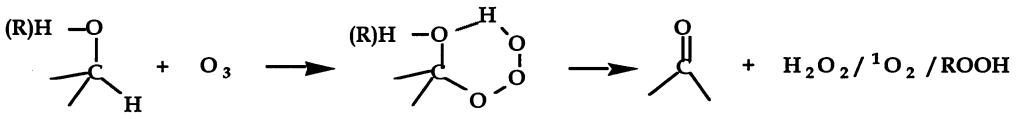
Ozone Selectivity

The strength deficiencies seen in pulps that have been bleached with ozone, and other oxygen-based bleaching systems, have their origin in greater amounts of cellulose chain cleavage reactions that effectively reduce the degree of polymerization (DP). The loss in DP is likely related to cellulose attack by ozone directly or by radicals. Further, there are three potential sources of radicals in bleaching conditions: (1) decomposition of ozone, (2) decomposition of reactive carbohydrate intermediates produced by ozone, or (3) decomposition of reactive lignin intermediates produced by ozone. Each of these four possibilities is discussed below.

Direct Reactions With Carbohydrates

Carbon-hydrogen bonds are susceptible to ozone cleavage, including the activated anomeric carbon-hydrogen bonds in carbohydrates. Highly reactive hydrotrioxide intermediates are produced from the ozonation of acetals,[4-6] including glucosidic acetals.[7-9] When there is an oxygen atom adjacent to the insertion site, the hydrotrioxide may be stabilized by an intramolecular hydrogen bond, forming a six membered ring (Equation 1). Several mechanisms have been proposed for the formation of the hydrotrioxides, in-

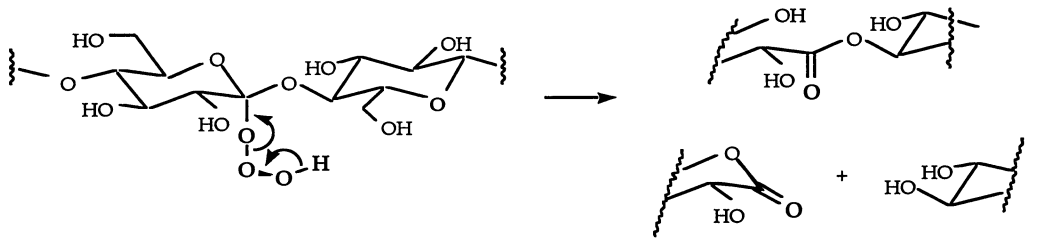
cluding a concerted 1,3-dipolar insertion, hydride transfer, hydrogen abstraction, and an initial attack at an acetal or ether oxygen. However, most kinetic data, solvent effects, substituent effects, stoichiometry, and thermochemical calculations support either the concerted insertion[4,10-12] or the hydride transfer.[10,13] Radicals are not likely to arise during the formation of hydrotrioxides, but may result from hydrotrioxide decomposition or other reaction pathways.[10,13]



(Eq. 1)

Once the hydrotrioxide intermediates are formed, they may decompose by ionic and/or radical pathways. The amount of ionic decomposition pathways depend on the other substituents on the hydrotrioxide-bearing carbon, solvents, and other reactants; products can be either carbonyls and hydrogen peroxide, carbonyls and singlet oxygen, alcohols and singlet oxygen, or carbonyls and alkyperoxyl compounds (Equation 1).[6,14] Homolytic (radical) cleavage is discussed under sources of radicals in ozone reactions.

The major products from ozonation of β-methyl glycosides in aqueous solutions are gluconolactone and gluconic acid.[8] A decomposition pathway for the hydrotrioxide has been proposed; the glycosidic bond is cleaved, rather than the ring oxygen bond, to form gluconolactone which subsequently hydrolyzes to form gluconic acid. These two β-glycoside reaction mechanisms are illustrated in Equation 2. Pan et al.[8] ozonated β-methyl glucoside and found glucose as a minor product. Katai and Schuerech proposed that ozone directly attacks the glycosidic oxygen to form a tetroxide intermediate, which then decomposes to glucose via a carbocation intermediate and unspecified degradation products of the tetroxide.[15]



(Eq. 2)

It is interesting that the methyl ester of gluconic acid was not identified in any of the aqueous reactions of ozone with methyl glycosides, in contrast to the nonaqueous reaction results of Deslongchamps et al.[7] Possible reasons include a lack of identification of this compound in the reaction mixtures, acid hydrolysis of the ester with a subsequent lactonization of the gluconic acid, or a solvent-mediated shift of the optimal reaction pathway.

Measurements of functional group concentrations in ozonized cellulose from pulp have shown that ozone only moderately increases carboxylic acid groups while carbonyl concentrations tend to fluctuate, but generally increase.[2,15-18] Most of the carbonyl compounds are ketones. While these general trends are similar in most studies, it should be noted that the ratios of carboxylic acids to carbonyl compounds were different. These differences illustrate the difficulties in ascertaining the dominate reaction pathways of carbohydrate degradation. The equilibrium between chain esters, lactones, and acids, coupled with the analytical difficulty in differentiating the carbonyl functional groups in complex mixtures, make elucidation of the direct mechanism of ozone degradation of cellulose challenging.

Introduction of carbonyl groups seriously affects the alkaline stability of carbohydrates, as well as color reversion. Carbonyl groups at C1, C2, and C3, have been implicated in the susceptibility of ozonated pulp to degradation during alkaline extraction stages. The low apparent viscosity of ozonated pulps, relative to strength properties, has also been attributed to carbonyl groups produced by ozone; peeling-type reactions occur during the alkaline viscosity assay. By contrast, oxidation of C1 and C6 to acid groups stabilizes carbohydrates towards hydrolysis, inhibiting further degradation. Reduction of carbonyl groups to alcohols retards degradation of O_3-treated pulps.

Radicals via Ozone Decomposition

The high reactivity of ozone results in its ready decomposition in protic solvents such as water. These reactive intermediates can then undergo complex chain reactions. Important decomposition reactions are given in Equations 3-11. Conditions that limit ozone decomposition include high ozone concentrations in solvents, low pH, and an absence of metals. The influence of these parameters can be understood by examining Equations 3-7. With high concentrations of hydroxide ion and water (i.e., alkaline pH, low ozone concentrations), decomposition reactions are kinetically favored. Metals such as cobalt, ferrous ion, ferric ion, manganese, and copper enhance ozone decomposition.[8] At pHs below 7, metal catalyzed decomposition is favored, while above pH 7, hydroxide-initiated reactions predominate.[19] Some additives may inhibit ozone decomposition by interfering with metal catalyzed decomposition[20] or by consuming radicals in chain termination reactions. The two most important consequences of ozone decomposition are inefficient consumption of ozone and the production of the highly reactive, unselective hydroxyl radicals (HO•), perhydroxyl radicals (HOO•), and superoxide radicals ($O_2^{\bullet-}$).

$$O_3 + OH^- \rightarrow O_3^{\bullet-} + HO^- \quad \text{(Eq. 3)}$$

$$O_3 + OH^- \rightarrow O_2^{\bullet-} + HO_2^- \quad \text{(Eq. 4)}$$

$$O_3 + OH^- \rightarrow O_2 + HO_2^- \quad \text{(Eq. 5)}$$

$$O_3 + H_2O \rightarrow O_2 + 2\,HO^- \quad \text{(Eq. 6)}$$

$$O_3 + H_2O \rightarrow 2\,HO_2^- \quad \text{(Eq. 7)}$$

$$O_3 + HO_2^- \rightarrow 2\,O_2 + HO^- \quad \text{(Eq. 8)}$$

$$O_3 + HO^- \rightarrow O_2 + HO_2^- \quad \text{(Eq. 9)}$$

$$O_3 + O_2^{\bullet -} \rightarrow O_3^{\bullet -} + O_2 \quad \text{(Eq. 10)}$$

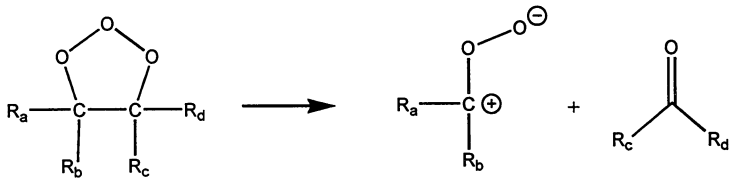
$$O_3 + HO_2^- \rightarrow O_3^{\bullet -} + HO_2^- \quad \text{(Eq. 11)}$$

Radicals from Reactive Intermediates

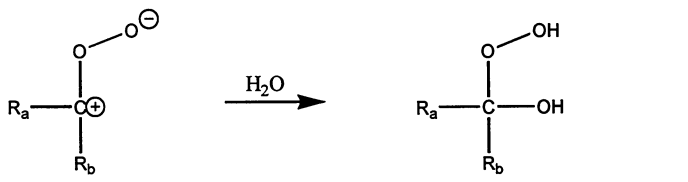
The hydrotrioxides from direct reactions of ozone with carbohydrates can undergo homolytic cleavage of oxygen-oxygen bonds to form either alkyperoxyl and hydroxyl radicals or alkoxyl and hydroperoxyl radicals (Equation 12). The radicals can further decompose, abstract a hydrogen, or couple. The radical decomposition reactions may not occur as readily as the ionic mechanisms in some instances;[6,14] however, they may initiate the formation of radicals that can play an important role in subsequent degradative chain reactions.

$$\text{R-O-O-O-H} \rightarrow \text{R-O-O}\bullet + \bullet\text{O-H} \quad \text{or} \quad \text{R-O}\bullet + \bullet\text{O-O-H} \quad \text{(Eq. 12)}$$

Additional reactive intermediates are likely to result from the reactions of ozone with lignin. The strong electrophilic properties of ozone allow it to react efficiently and rapidly with sites of high electron densities in lignin, such as double bonds in the side chain and the aromatic rings. The reaction pathway that is most likely to predominate in aqueous ozone bleaching is decomposition of a primary ozonide to carbonyl and carbonyl oxide fragments. The latter is trapped by water to form an α-hydroxy hydroperoxide. The fate of the hydroperoxide depends on other substituents, solvents, and other reaction conditions; however, this structure is susceptible to homolytic cleavages similar to that of hyrogen peroxide and hydrotrioxides.



a primary ozonide — a carbonyl oxide — a carbonyl



an α-hydroxy peroxide

Additional lignin intermediates may also serve as radical precursors. Balousek et al.[21] ozonated a β-aryl ether model compound and found products that supported a reaction in which the ozone inserts into the β C-H bond, forming a hydrotrioxide intermediate. They proposed a homolytic decomposition pathway to a hydroperoxy radical and a ketone, analogous to a mechanism reported by Plesnicar et al.[14] for α-methyl benzyl ethers and alcohols. It is noteworthy that the insertion reaction was competitive with the rapid reactions with electron-rich alkenes and aromatics; it might be predicted to have a considerably slower reaction rate. However, if the lignin insertion reaction occurs under bleaching conditions, it is likely to effectively depolymerize those portions of the residual lignin macromolecule that still retain β-aryl ethers after cooking.

The hypothesis that lignin intermediates may be the source of radicals that deteriorate carbohydrates during ozone bleaching is supported by the recent work of Griffin, et al.[22] They have proposed a model of ozone delignification whereby an advancing front of lignin-ozone reactions takes place across the cell wall to the lumen. The authors suggest that hydroxyl radicals are produced by the ozone-lignin reactions and that the radicals immediately degrade the adjacent carbohydrates; thus, all cellulose decomposition takes place within the ozone-lignin front.

Radical Reactions with Cellulose

The radicals of most concern are hydroxyl radicals (HO•), perhydroxyl radicals (HOO•), and superoxide radicals ($O_2^{\bullet-}$). Of particular importance is the hydroxyl radical, which is very reactive with both lignin and carbohydrates.[23-27] In their reactions with wood components, hydroxyl radicals can produce organic radicals (R•), peroxides (ROOR) and hydroperoxides (ROOH) (Eq. 13-15).[28] The secondary radicals can serve as chain carriers, promoting further decomposition reactions.

$$HO\bullet + H\text{-}R \rightarrow HOH + \bullet R \qquad \text{(Eq. 13)}$$

$$R\bullet + O_2 \rightarrow ROO\bullet \qquad \text{(Eq. 14)}$$

$$ROO\bullet + H\text{-}R \rightarrow ROOH + \bullet R \qquad \text{(Eq. 15)}$$

Hydroxyl radicals react indiscriminately with both lignin and carbohydrates. Ek, et al., studied the reactions of hydroxyl radicals with lignin and carbohydrate models; the rate constants are approximately the same (Table 1).[24] Hydroxy radicals react with carbohydrates by hydrogen abstraction to form hydroxy-alkyl radicals that subsequently are captured by oxygen to form carbonyl compounds. The carbonyl compounds are precursors to chain cleavage and peeling reactions that result in poor pulp quality and low yields, respectively.[29] Effective bleaching strategies must preserve the high degree of polymerization and crystallinity of cellulose in order to preserve pulp strength properties.

Table 1. Rates for hydroxyl radicals reacting with lignin and carbohydrate models.[24]

Compound	Rate constant $(M \cdot s)^{-1}$
Veratrylglycol	1.5×10^{10}
Veratrylglycol-β-guaiacyl ether	1.7×10^{10}
Methyl-β-D-glucopyranoside	3.2×10^{9}
Methyl-β-D-xylopyranoside	2.6×10^{9}

Radical versus Direct Reactions with Ozone

In comparison to HO•, ozone appears to be much more selective in its reactions with lignin and carbohydrate models.[30-34] The reactivity of ozone was reported to be 5 to 6 orders of magnitude greater for lignin-like compounds than for carbohydrate-like compounds(Table 2).[31] It has, therefore, been suggested that radicals from ozone decomposition are responsible for ozone's low selectivity in water.

Table 2. Reaction rate constants for select ozone reactions.[31]

Compound	Rate constant $(M \cdot s)^{-1}$
Styrene	$>10 \times 10^{4}$
p-Cresol	3.0×10^{4}
Glucose	0.5
Saccharose	0.1

However, the effect of hydroxyl radicals in carbohydrate degradation during ozone bleaching appears to be extremely variable and dependent on specific reaction sequences and pulps. Metals decompose ozone and peroxide to radicals, including hydroxyl radicals. Spiking pulp-ozone mixtures with metals induces carbohydrate degradation.[16] Conversely, acid washing and chelation to remove metals prior to ozonation will improve ozone selectivity, in some instances.[34]

However, not all data indicate that the hydroxyl radical is the sole species responsible for cellulose degradation. Ni, et al. compared the cellulose degradation caused by O_3 and by HO• generated from the decomposition of peroxide with Fe^{2+} ions (Fenton's Reagent).[35] The results (Table 3) suggest that hydroxyl radicals play only a small role in the ozone degradation of cellulose. Approximately one-third of the viscosity loss could be attributed to hydroxyl radicals. High consistency (30%) ozonation of pulp with and

Table 3. Comparison of carbohydrate degradation caused by ozonation and by generated hydroxyl radicals.[35]

Ozonation		Fenton's Reagent	
Ozone Charge (%)	Viscosity (cP)	Peroxide charge (%)	Viscosity (cP)
0	21.3	0	21.3
0.3	11.7	0.3	19.0
0.6	8.1	0.6	17.6
1.0	7.4	1.0	17.4

without 5% methanol addition were also performed.[35] A small increase in selectivity was noted with 5% methanol addition. Cellulose degradation still occurred; the investigators concluded that the formation of radicals from ozone was not the main reason for low selectivity.

The effect of various solvents on O_3 selectivity has also been examined. The selectivity increases in the presence of 90% acetic acid in the bleaching of softwood kraft pulps; the effect was attributed to the radical scavenging ability of acetic acid.[30] However, other factors may be involved; O_3 is ~10 times more soluble in acetic acid than in water.[36] The increased ozone solubility facilitates the transport of ozone inside the fiber. Acetic acid is also known to sequester metal ions.[35,37] Deactivation of metals by acetic acid may help prevent the decomposition of ozone into radical species.

Jacobson, et al. report that O_3 selectivity is better in 50-100% methanol than in pure water; they postulate that methanol acts as a radical scavenger.[38] Xu, et al. have shown that methanol and *t*-butanol, at a 0.8 M level, improved the selectivity of the low consistency (~1.2%) ozonation of unbleached kraft pulps.[36] Zhang, et al. report that carbohydrate models are degraded less with ozone when methanol, *t*-butanol, and acetic acid are present, versus 100% water; they suggest that both direct ozone attack and indirect HO• attack of carbohydrates are important degradation routes, leading to low selectivity.[32,33] In their latest report, the University of New Brunswick group indicate that O_3 selectivity increases with increasing organic solvent concentration, and lower temperatures.[39] The protective action of the organic solvent is greater when lignin is present; the researchers suggest that hydroxyl radicals might be generated from lignin/ozone reactions and lead to greater carbohydrate damage when lignin is present.

It is clear that the role of radicals in carbohydrate degradation during ozone bleaching under various conditions remains to be resolved.

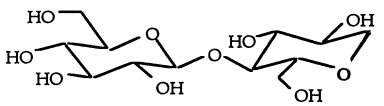
Experimental Plan

Selectivity Measurements

Selectivity measurements for pulp samples rely, to a first approximation, on determining the ratio of the change in kappa number to the change in viscosity during ozonation. While this seems simple, there are problems associated with both the observed kappa number and viscosity. A sample containing partially oxidized lignins will display a lower pulp kappa number than non-oxidized lignin. The viscosity, which is related to carbohydrate DP and paper strength,[40] frequently varies, in an unexplainable way, with the process.[41]

A much less structurally complex model system would allow us to follow various degradation reactions and develop an in-depth understanding of selectivity changes. Previous model studies have touched upon this fact, but have not been taken to the depth needed for a good understanding of the mechanisms involved. The carbohydrate model most often studied has been a very simple structure, such as methyl-β-D-glucopyranoside and here the rate of disappearance was the main interest. This model was frequently used in early studies of the mechanism of carbohydrate chain cleavage reactions.[42] However, the model has several limitations; it is a monosaccharide with an atypical glycosidic substituent. There is much less steric hindrance to attack at C-1 and frequently attack is observed at the methyl group. A better model, more representative of cellulose, is 1,5-dianhydrocellobiitol (**1**) and related compounds.[42] The advantage of **1** is that it is a disaccharide model that resists "peeling" reactions and more closely resembles the environment around the β-(1-4) linkage that holds cellulose monomers together. The reactions of such a model have yet to be studied with ozone.

Our intent is to study more representative cellulose models, and even cellulose itself. We will first use the relatively simple model, 1,5-dianhydrocellobiitol (**1**), to explore reaction sites and product compositions. Our goal is to develop methods with models that can be applied to the more complex cellulose case. For example, we want to determine the location and frequency of carbonyl and carboxyl introduction with **1** and then apply those same techniques to cellulose. The introduction of carbonyl groups (a functional group that would weaken the polymer) by ozone can be determined by (1) NMR spectroscopy and (2) reducing the carbohydrate with sodium borodeuteride and examining the level and position of deuterium incorporation in the hydrolyzed products.



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The best cellulose model is cellulose itself, particularly amorphous cellulose. We believe that the selectivity of bleaching reactions can be effectively monitored by exam-

ining the effects that bleaching chemicals have on amorphous cellulose and on mixtures of amorphous cellulose and a lignin model compound. Specifically, we will examine (1) viscosity and molecular weight changes of amorphous cellulose to determine differences in polymer chain length, and (2) the extent of degradation to a lignin model to determine pulp delignification efficiencies. For cases of cellulose damage, we will further examine structural changes in the cellulose.

Why study amorphous cellulose? Amorphous, or disordered, regions are much more accessible to reagents than are crystalline (highly structured) regions.[43] The main reactions of wood carbohydrates may be at amorphous regions; the severe loss of hemicelluloses during pulping is probably strongly related to the amorphous nature of this polymer. The reactivity difference between "peeling-resistant" crystalline and amorphous cellulose samples, as obtained in our laboratory (Figures 1 and 2),[44] indicate much greater viscosity losses for the latter. The apparent small increase in viscosity for the reaction of hydrogen peroxide with crystalline cellulose in Figure 1 may reflect selective removal of low molecular weight polymers.

A peeling-resistant amorphous cellulose appears to be an ideal substrate for studying bleaching selectivity since harmful chain cleavage reactions of the carbohydrates are magnified and readily recognized. However, looking at carbohydrate damage is only half of the "selectivity" issue. Lignin degradation is the other half. Recent mechanistic studies show the value of examining wood component reactions in the presence of other wood components. For example, Abbot and Brown observed that magnesium ions promote decomposition of hydrogen peroxide; when cellulose was present, the decomposition was suppressed.[45] Similar unusual effects were observed in the presence of vanillin (a lignin model). Therefore, it is apparent that proper model systems are needed to arrive at accurate conclusions about bleaching chemistry.

The ideal model system for studying selectivity on the molecular level would be a lignin model dimer bound through a chemical linkage to the amorphous cellulose. Such a substrate would represent a suspected residual lignin material in pulp known as a "lignin-carbohydrate complex (LCC)."[46] However, such a model is not available at this time. The next best model would be a mixture a polymeric lignin model[47] and amorphous cellulose; this mixture mimics pulp since both lignin and cellulose are undissolved before degradation reactions set in. Reactions of the mixed polymer model system will be a focus area in our proposed research; both components are available in our laboratories.[44,47]

In addition to this mixed polymer system, we will examine a mixture of lignin model monomer or dimer in the presence of amorphous cellulose. Most lignin monomer and dimer models are relatively insoluble in water under the acidic conditions employed during ozone bleaching. This could present a problem in generating representative lignin since the models may associate and, thus, be less accessible (in comparison to actual lignin). Previous studies have used simple models, such as veratrylglycol-β-guaiacyl ether, in a mixture of water and organic solvent to obtain a homogeneous solution. The problem here is two-fold: (1) the model is soluble, while lignin is not during ozonation,

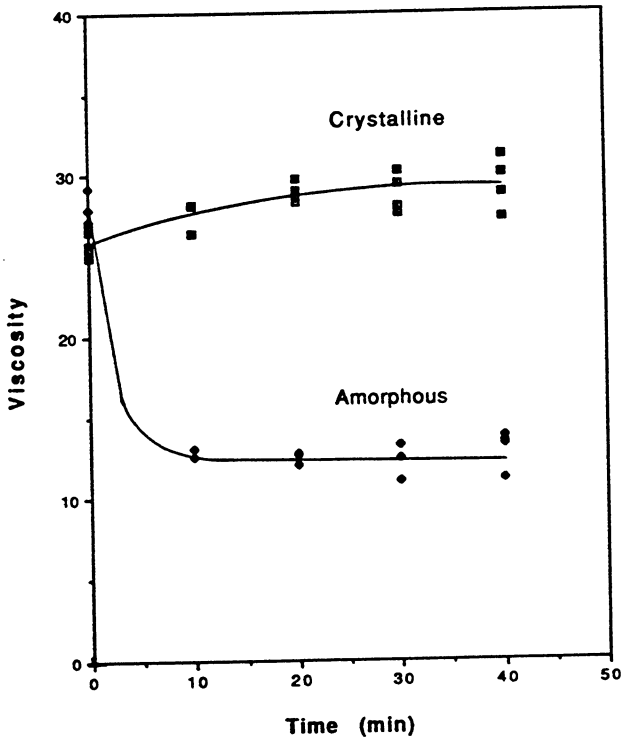


Figure 1. Viscosity vs time profile for the reaction of crystalline and amorphous celluloses with 0.2% H_2O_2/0.1% NaOH at 12% consistency at 50°C.[44]

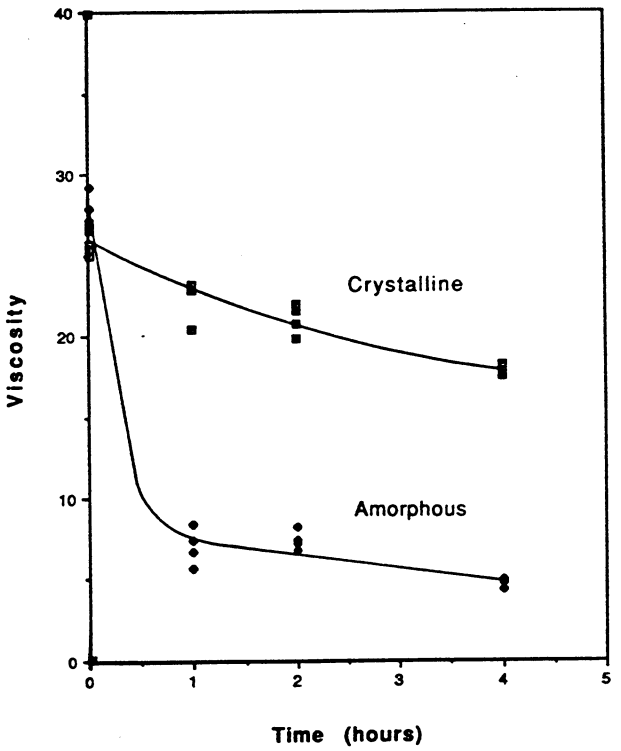
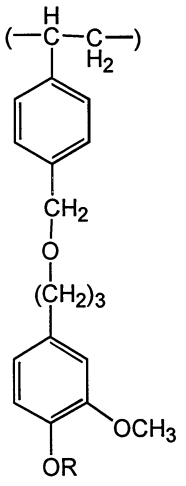


Figure 2. Viscosity vs time profile for the reaction of crystalline and amorphous celluloses with O_2 in 0.1N NaOH and with 0.3 mmol cobalt ions at 100°C.[44]

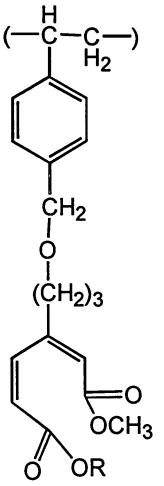
and (2) the organic solvent can scavenge radicals and greatly affect the reaction mechanism. Care will be taken by us to adequately disperse the model with the amorphous cellulose. It may be possible to develop "intimacy" between the lignin model and cellulose by adding the lignin model to the cellulose solvent that is used to generate amorphous cellulose. In one case, we will examine the reaction of a soluble lignin model in the presence of amorphous cellulose.

The polymeric lignin model that we plan to study is a simple phenyl propane structure bonded to polystyrene (**2**).[47] The model has two types of aromatic rings; however, the oxygen-substituted (lignin model) ring should be much more reactive towards O_3. The polymeric lignin model can be manipulated to resemble either phenolic or nonphenolic lignin. This can be done by partially (or completely) methylating the phenolic hydroxyl groups of **2** with diazomethane to give **3**.

For reactions of the polymeric model mixture with ozone, we will be looking for (a) molecular weight changes and carbonyl introduction in the amorphous cellulose and (b) the production of muconic acid structures (**4** and **5**) and degradation products from the lignin model. For this and other lignin models, we will characterize as many of the lignin degradation products as possible. The degradation of a lignin model absorbed onto cotton linters with ozone in water has recently been studied at IPST; therefore, some of the preliminary investigations are complete. We have also developed techniques for the identification of carbonyl and polyfunctional carbonyl compounds.[48]



2, R = H
3, R= CH_3



4, R = H
5, R= CH_3

Various chromatography techniques will be employed to isolate lignin model reaction products. The components will be characterized by mass (MS) and nuclear magnetic resonance (NMR) spectroscopy. The residual model will be examined directly by solid state NMR and FTIR[47] and/or by liquid state NMR after isolation. All the necessary modern instrumentation is on hand. Analysis of the level of muconic acids may be

possible by acid/base titration techniques. Unlike pulp, the model systems can use larger quantities of "lignin" to help facilitate the isolation and spectral investigations.

Selectivity Issues for Direct Ozone Attack

We will ozonize 1,5-dianhydrocellobiitol and pure amorphous cellulose in the absence of metals and in the presence of radical scavengers; direct ozone reactions will be favored under such conditions. Reaction products will be identified and quantified, together with changes in polymer DP. In addition to the techniques already described, we will use GC to quantify and GC-MS and NMR to help identify reaction products. The observed carbohydrate degradation could be a result of direct attack by O_3 or a result of secondary radicals reactions, initiated by decomposition of hydrotrioxide intermediates, etc. To determine the role of carbohydrate-derived radicals on carbohydrate degradation, we will follow the course of the reaction with time. Changing product composition over the course of the reaction indicates a change in reaction mechanism. One explaination for a changing reaction mechanism would be that the initial products are a result of direct attack by O_3, while the slower developing products are due to by-products, such as ozone, carbohydrate, or lignin radical species.

We intend to study hydroperoxide/carbohydrate chemistry by mixing the hydroperoxide of dioxane (commercially available) with 1,5-dianhydrocellobiitol and amorphous cellulose under typical ozone bleaching conditions and follow the extent and type of reaction that occurs. The structure of dioxane hydroperoxide should be similar in reactivity to that of carbohydrate hydroperoxides.

Selectivity Issues for Radicals Derived from Ozone

To determine the role of radicals derived from ozone decomposition, we will expose 1,5-dianhydrocellobiitol and amorphous cellulose (with and without lignin models present) to hydroxyl radicals. The latter will be generated from hydrogen peroxide and Fenton's reagent. Ni has studied HO•/pulp reactions in this manner.[35] While Ni's focus was on viscosity changes, our focus will be on chemical structure changes. The extent of degradation will be measured, and the products of model studies will be identified and quantified, primarliy by GC, GC-MS, and NMR. It is expected that hydroxyl radicals will be much less discriminating in their reactions and, thus, provide a different set of products than that obtained from direct ozone reactions. We anticipate that HO• will react to give carbonyl incorporation at nearly all -CHOH sites, while O_3 will prefer reaction at C1. As appropriate, other radical species may also be investigated.

Selectivity Issues for Radicals Derived from Lignin

To determine the role of lignin-derived radicals on carbohydrate degradation, we plan to ozonize 1,5-dianhydrocellobiitol and amorphous cellulose in the presence of

lignin models and isolated lignin. The extent of lignin reaction with ozone will be compared to the degree to which 1,5-dianhydrocellobiitol and amorphous cellulose are degraded. The DP of amorphous cellulose will be followed by viscosity and GPC. Reaction products will be identified, quantified, and compared to those obtained without lignin. If we find, for example, that the product (carbonyl introduction) distribution with amorphous cellulose is the same as that observed when amorphous cellulose is allowed to react with dioxane hydroperoxide, we can infer that hydroperoxides play a role in cellulose degradation. We will examine different lignin/cellulose ratios and reaction conditions, the effects of addition of hydroperoxides, and the influence of lignin structure (phenolic, non-phenolic, partially oxidized, etc.).

General Selectivity Issues

Bleaching selectivity depends on oxidant type and reaction conditions, including pulp consistency, oxidant concentration, pH, time, temperature, filtrate carry-over, mixing, solvent composition, and the presence of metals and additives.[34,49] In a thorough study of bleaching selectivities researchers need to consider all these factors. However, we will *limit* our study to those variables that are expected to be the most critical. A particularly important variable for study is the influence of metal ions in the ozonolysis reactions. In our model system, we should be relatively free of metal contamination. Consequently, the best way to study metal effects is to add specific metals to the reaction medium. Among the experiments envisioned are determinations of rate constants for both delignification and carbohydrate degradation reactions and generation of selectivity curves under different conditions.

If time permits, ozone treatments will be applied to a mixture of amorphous cellulose and a soluble lignin model; the information generated will reflect on the importance of secondary reactions. The latter term in this context refers to reactions of ozone with dissolved materials that are released from the pulp during bleaching. Control of secondary bleaching reactions is an important way to maximize the efficient use of ozone; the differences in product yields and reaction rates of soluble and insoluble model systems may provide insights on how to best use ozone.

The model studies will provide the information necessary to predict appropriate changes to optimize the ozone bleaching of pulps.

Rationale and Significance

Alternative nonchlorine bleaching technology must evolve in order to meet new environmental regulations, new customer demands, and new ways to achieve mill closure. Mill closure is the key to solving the major environmental concerns associated with bleach mill effluent. Bleaching in a totally chlorine-free (TCF) manner could be the simplest way to achieve mill closure, since the bleach effluent should be non-corrosive when burned. However, the use of strictly oxygen-based bleaching stages has a negative

impact on pulp quality. A viable alternative would be to use a more selective bleaching reagent, chlorine dioxide, at levels where chlorine liquor components can be controlled enough to minimize corrosion. This will be difficult to achieve in a cost effective way with high levels of ClO_2, i.e., a DE(OP)DED bleaching sequence; however, it may be possible to achieve with replacement of one or more D stages with ozone.

Through this research, we are attempting to develop a detailed understanding of selectivity issues associated with ozone bleaching. The information will lead to (1) a greater fundamental understanding of cellulose depolymerization processes and (2) new ways to produce high strength, high brightness paper products. Improvements in ozone bleaching will help the development of new strategies to reduce the level of discharged wastes. In addition, better control of carbohydrate degradation will lead to higher pulp yields and the need for less fiber for a given paper.

Progress to Date

Preparation of Amorphous Cellulose

Amorphous cellulose is prepared by dissolving cellulose substrate, such as cotton linters, in a suitable solvent system and then diluting with a non-solvent to obtain amorphous cellulose. Three solvent systems have been studied and the results of those studies are described below.

I. SO_2/DEA/DMSO

Sulfur dioxide has been used as a derivitizing agent for the dissolution of cellulose in dimethylsulfoxide (DMSO) in the presence of diethylamine (DEA).[50] According to the literature, solutions of cellulose (2.7 % w/w) were obtained in a matter of minutes from the SO_2/DEA/DMSO system. We did not find this to be the case for our experiments. We had a very difficult time getting the cotton linters to dissolve, even when the linters were allowed to swell and disperse in DMSO prior to SO_2/DEA addition. In the cases in which the cellulose did fully dissolve (after 24 h of SO_2/DEA contact) the resulting cellulose had such a low DP, as indicated by a viscosity of 3 cP, that the amorphous cellulose was deemed useless for future studies. Because of these problems, this method of dissolution was abandoned.

II. NMMO•H_2O/DMSO

N-Methylmorpholine N-oxide (NMMO) has been reported[51-55] as a good cellulose solvent, both in its anhydrous form and as a monohydrate (NMMO•H_2O). However, the anhydrous form of the solvent has a melting point close to its decomposition temperature, which makes use of anhydrous NMMO potentially hazardous, and thus, undesirable. On the other hand, if more than 2.5 equivalents of

water are present in the NMMO, then all of the interactive sites on the solvent (hydrogen-bonding sites) are occupied by water, and thus, the NMMO cannot dissolve the cellulose. Solutions of up to 15 % cellulose have been obtained using NMMO•H_2O. DMSO can be used in conjunction with NMMO•H_2O to completely destroy the crystalline texture of cellulose (DMSO/NMMO/H_2O = 10/1/1). We have successfully dissolved cotton linters in NMMO•H_2O. However, addition of 10 equivalents of DMSO (relative to NMMO) to the cellulose solution did not result in complete homogeneity as noted by the presence of a gel.[54] In other words, the DMSO did not diffuse readily into the NMMO•H_2O/cellulose solution. Since the crystallinity of the sample was questionable, and since a 50 % DP reduction was expected,[51] we decided to pursue another solvent in lieu of further investigating the DMSO/NMMO/ H_2O solvent system.

III. LiCl/DMAc

Dimethylacetamide (DMAc) containing lithium chloride (5-9 %) is known to be a good solvent system for cellulose.[55-58] Importantly, it is a nondegrative solvent, and solutions of cellulose can actually be stored for extended periods of time in LiCl/DMAc if desired. The maximum concentration of the cellulose solution is dependent on DP. Solutions containing 12 % 550 DP cellulose and 10 % LiCl in DMAc were obtained in 4-6 h while at a higher DP of 1700, only 4 % cellulose solutions could be prepared.[55] We have successfully dissolved cotton linters in 9 % LiCl/DMAc at 0.5 % (w/w) concentrations. The resulting cellulose solution was poured onto a 50/50 mixture of water/methanol. Cellulose beads obtained by drop-wise addition of the DMAc solution into a non-solvent have been reported to maintain their amorphous texture (i.e., no detectable x-ray diffraction).[58] Amorphous cellulose has been obtained reproducibly in 4 g (dry weight) batches. The procedure is simple and has only two disadvantages: first, the entire selling, dissolution, and washing processes require approximately one week to complete and, second, DMAc is known to cause spontaneous abortions in pregnant women so, as a precaution, no females are allowed to work with DMAc in our labs. The LiCl/DMAc procedure appears to be the simplest, reproducible, nondegrative solvent system for cellulose. This method for amorphous cellulose preparation will be our method of choice.

Reactions with Ozone

I. Cellulose Models

1,5-dianhydrocellobiitol (**1**) has been allowed to react with ozone in the presence of acetic acid (a radical scavenger). To date, ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy has not shown evidence of any reaction between ozone and the cellulose model. Since the detection limits of ^{13}C NMR are such that

only 5% or greater product yield can be detected, methods are currently being developed to use gas chromatography (GC) to analyze the reaction mixture. Initial studies indicate that acetylation of the reaction mixture with acetic anhydride in the presence of pyridine will yield volatile products that can be analyzed by GC and mass spectrometry (MS).

Methyl β-D-glucoside (MβG) was also allowed to react with ozone in the presence of acetic acid. By ^{13}C NMR, no evidence of reaction was observed. GC is expected to be a more sensitive technique for the observation of small quantities of products and will be explored in the near future. Also, to date, only a small excess of ozone has been applied to MβG (100-200 % charge). Extensive ozonation should lead to more reaction.

II. Amorphous Cellulose

Amorphous cellulose (from solutions of LiCl/DMAc) was allowed to react with ozone in aqueous acetic acid. Extensive depolymerization was observed as noted by the large quantity of water soluble products obtained after the reaction. We are currently developing gel permeation chromatography (GPC) techniques to determine the extent of DP loss. We have attempted to obtain viscosities in cupriethylenediamine (CED) in a manner analogous to pulp viscosity measurements. However, this has not been successful due to the lack of solubility of the amorphous cellulose in CED. It is possible that the cotton linters have such a high DP, even after reaction with ozone, that complete dissolution in CED is not possible at the concentrations described for the standard Tappi procedure for pulp samples.

III. Ozone Experimental Design

The flow of ozone in oxygen from the ozone generator is split into two lines. One line (a blank) passes directly into a potassium iodide (KI) trap which is then titrated with sodium thiosulfate. The other line passes through a solution of the sample in a gas washing bottle and then to a KI trap. The amount of ozone absorbed by the solution in the gas washing bottle can be calculated from the relative flow rates of the two lines in addition to the information obtained from the two KI/thiosulfate titrations (one from the blank, one from the sample).

The amount of ozone remaining in solution can be obtained by ultraviolet (UV) absorption measurements at 260 nm. (The UV absorportion and ozone concentration have a linear relationship.) Theoretically, if none of the ozone in the gas washing bottle reacts, the concentration of ozone in solution, as obtained by UV, should be equal to the difference in ozone in the blank KI trap and the sample KI trap. This is not the case in our experiments. We do not have a good mass balance of ozone between the KI titrations and the UV absorption measurements. We are currently exploring whether or not the ozone is efficiently trapped by the KI solutions.

Since the half-life of ozone in solution is approximately 30 min., decomposition of the ozone should not contribute significantly to the ozone loss. Reaction of ozone with substrates in the gas washing bottle also should not seem to account for the poor material balance. The mass balance problem must be solved before we do any detailed mechanistic ozonation experiments.

Project Tentative Schedule

Last March we proposed a tentative schedule for the completion of our research. The USDA only granted 70 % of the requested funding. Therefore, we modified our Project Tentative Schedule, as shown in Table 4, before the project began in mid-October. We are simultaneously working on sections 1A and 1B of the table now.

Table 4. Project Tentative Schedule (time in months)

Time	Activity
8	1. Ozone reactions in the presence of radical scavengers A. with 1,5-dianhydrocellobiitol (**1**); determine - extent of reaction at C-1 leading to dimer-monomer conversion - extent of CHOH to C=O conversion; location of C=O groups - applicability of NMR, GC-MS, and FTIR spectral techniques - applicability of deuterium-labeling techniques B. with amorphous cellulose; determine - extent of depolymerization; development of GPC techniques and correlation to viscosity measurements - other analysis as in 1A C. with styrene polymeric lignin models **2** and **3**; determine - extent of depolymerization; analysis by GPC and NMR - extent of aryl to muconic acid conversion by titration and NMR - soluble products by GC-MS
6	2. Selectivity of direct ozone attack (presence of radical scavengers) A. with different ratios of 1,5-dianhydrocellobiitol/styrene polymeric lignin model mixture - determine extent of reaction with each substrate and changes in product distributions compared with that observed in Section 1 B. with different ratios of amorphous cellulose/styrene polymeric lignin model mixture - determine extent of reaction with each substrate and changes in product distributions compared with that observed in Section 1 - develop a GPC/viscosity technique for the mixture that provides information on the change in DP for the amorphous cellulose

Thus far, we have not observed any reaction of 1,5-dianhydrocellobiitol (**1**) with ozone. Conditions will be varied to favor reaction of model **1** with ozone. The current procedure to identify the location of carbonyl groups is to isolate the individual products and characterize them by MS, FTIR, and NMR. We have the technology and equipment to do this, but it is a very time consuming and tedious process. We need to reconsider the value of the location of carbonyl groups against the time it will take to identify each product of the model studies. However, once the products are initially identified and characterized, the spectral information of any new compounds will be available for the first time to the scientific community at large. As far as deuterium labeling goes, we cannot perform sodium borodeuteride reductions unless we first observe some oxidation.

We have observed depolymerization of amorphous cellulose upon reaction with ozone. We have discovered that viscosity measurements are problematic in that the cotton linters do not dissolve readily in CED. CED is a somewhat degradative solvent to cellulose, so extended exposure of the cellulose to CED to aid dissolution also results in degradation of the sample undergoing analysis. GPC techniques are currently being developed. Before a sample can be analyzed by GPC, it must first undergo carbamylation (Eq. 16). Carbamylation is accomplished by addition of phenyliso-cyanate (**6**) to cellulose in pyridine.[57] The resulting carbamate **7** is THF and pyridine soluble and UV active. Cellulose is insoluble in pyridine. Therefore, the disappearance of insoluble material is an indication that the reaction is proceeding as desired. We expect to use THF as the mobile phase during GPC. We have experienced some difficulty obtaining fully carbamylated (i.e., fully soluble) material from the reaction shown in Eq. 16. We may need to resort to step-wise or multiple phenylisocyanate treatments to remedy this problem. Since the carbamylated product **7** should be UV active, detection of the cellulose products by GPC should be straight forward.

$$\underset{}{\text{Cellulose-OH}} + \underset{\mathbf{6}}{\text{Ph-N=C=O}} \xrightarrow[\text{pyridine}]{\Delta} \underset{\mathbf{7}}{\text{Cellulose-O-CO-NH-Ph}} \qquad \text{(Eq. 16)}$$

Recall that reactions of ozone with cellulose are only half of the selectivity problem when bleaching pulps. Reactions involving ozone with lignin are the other half. We are interested in studying the ozonations of lignin models such as guaiacol (a soluble model) and styrene polymeric lignin models **2** and **3** (insoluble models). We will study lignin models as this project develops.

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